













# THE FUNDAMENTALS OF QUANTITATIVE ANALYSIS

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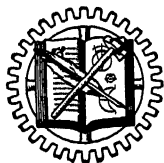
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## PREFACE

An inspection of the Table of Contents of this volume will suggest to those familiar with the author's Principles of Quantitative Analysis, the first edition of which was published in 1914, that it is essentially a revision of the former book. Although the titles of most of the chapters are the same or similar to those of the earlier volume two-thirds of them have been entirely rewritten and most of them have been amplified. This seems sufficient justification for giving the book a slightly different title.

The primary object of this, as well as the former book, is to present in some detail the theoretical and practical features of a series of exercises in Quantitative Analysis, which may form the basis of a year's course for students of college rank who have had at least one year's work in general chemistry. It seems to be generally conceded, that although the second year's work in inorganic chemistry should consist of quantitative exercises, the primary object of such a course is drill in the use of the fundamental principles of modern theoretical chemistry quite as much as the attainment of the ability to make quantitative determinations. The author therefore has found no reason to change the essential features of the method of presentation adopted in the former book, which is based upon a scheme of classification of quantitative processes in which the essential differences between different types of homogeneous and heterogeneous equilibria upon which such processes depend, are emphasized and the factors affecting them discussed.

The last section of the earlier volume, which deals with the use of physio-chemical processes, has been eliminated, since this part of the subject is sufficiently comprehensive to justify treatment as a separate volume, and in the author's experience it has been difficult to find time in a year's course to discuss them adequately.

It will be noted that the questions and problems, which, in

the author's opinion, form an essential feature of such a course, have been revised and increased in number. They cover a wider range of topics than an understanding of the laboratory work actually carried out demands, and are designed to develop the student's ability to deal with chemical processes in general and to avoid excessive emphasis of stoichiometry, which subject should offer no especial difficulty to properly prepared second-year students in chemistry. They are, for the most part, typical problems, which should be changed from year to year by the instructor, and therefore the answers to most of these which involve mathematical calculations have been given.

As noted in the preface to the former volume there is little that is novel in the matter here presented and the author takes pleasure in acknowledging his indebtedness to the many workers who have contributed to the subjects here discussed. Especial thanks are due Dr. Frederick D. Rossini, who read the revised manuscript and made a number of useful suggestions.

WALTER C. BLASDALE.

BERKELEY, CALIFORNIA,  
August 10, 1928.

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# FUNDAMENTALS OF QUANTITATIVE ANALYSIS

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## CHAPTER I

### INTRODUCTORY STATEMENTS AND DEFINITIONS

**Importance of Quantitative Analysis.** Quantitative analysis has for its object the determination of the quantity of some element or compound present in a particular substance. The result of the determination is usually expressed as a percentage, ordinarily by weight, but sometimes by volume, of the substance concerned.

The subject is of importance from a number of standpoints. An accurate evaluation of most of the important materials of commerce, and determination of their fitness for certain purposes, cannot be made until their quantitative composition has been determined. In many manufacturing industries the raw products used are purchased, and the finished products obtained are sold, on the basis of the results shown by their analysis; further, the entire process of manufacture is often controlled by means of analyses of the various products, for such analyses enable the manufacturer to determine whether each of the various stages of the process have been properly carried out, and to reduce wastes and losses to a minimum.

In the study of many branches of natural science the investigator is often obliged to depend upon quantitative analyses for the identification and comparison of the substances with which he is concerned, and is frequently enabled to trace the laws which govern the changes taking place in these substances through the study of the results of their analysis. The present science of chemistry is based very largely upon the employment of quantitative methods

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in the study of chemical changes; the sciences of geology and physiology have been very largely developed by the use of data gathered through the employment of quantitative methods.

The subject has also a certain educational value, in that it concentrates the attention of the student upon a limited number of chemical transformations; teaches him to observe critically all of the changes which take place in the material with which he is dealing, and to devise methods of avoiding certain undesirable effects and take advantage of others which are desirable.

**Range of the Subject.** It is evident from the preceding paragraphs that the field of quantitative analysis extends over an extremely wide range of subjects, for the analyst may be called upon to determine the quantitative composition of any material object whatever. The analysis of substances containing a number of constituents often presents a problem of much complexity, and much ingenuity has been used in devising methods, which can be employed to determine those elements and compounds, that are of importance from either a practical or scientific standpoint, with the requisite accuracy and with the minimum expenditure of time and effort. The acquirement of a working knowledge of even the more important of these methods is a task of considerable magnitude, and the subject forms one of the most comprehensive branches of the science of chemistry.

**Types of Quantitative Processes.** A sufficiently comprehensive and entirely satisfactory classification of all the methods included under the general head of quantitative analysis is not easily formulated. All of the more important methods in general use may be grouped under four classes, which differ so fundamentally in method of procedure that it is desirable to discuss them separately.

Gravimetric methods are those in which the determination is effected by the actual separation of the desired constituent, or some product which bears a definite quantitative relation to it, and the determination of the weight of the product thus separated. Thus the silver can be determined in an alloy by dissolving a definite weight of the alloy in nitric acid, separating the silver present as insoluble silver chloride, weighing the latter, and calculating the weight of silver present from the factor representing the

ratio of the atomic weight of silver to the molecular weight of silver chloride.

The distinguishing feature of all gravimetric processes is the mechanical separation of a product, the weight of which bears a known relation to the weight of the substance which is being determined, from the substance being analyzed. Such separations are possible only when there are definite surfaces, which represent the limits of the spaces occupied by the separated substance on the one hand, and the residual mixture on the other. Expressed in the language of modern theoretical chemistry every gravimetric process involves a series of chemical and physical operations, which bring about such changes in the original substance that a new "phase" separates, the term phase being used to designate a mass of matter which is physically and chemically homogeneous. In the illustration cited the separated phase took the form of a solid; it might have taken the form of a gas, or of a second liquid, which does not mix with the first, and a logical and convenient basis for the classification of gravimetric processes is found in the type of "phase-transformation" which they represent. Such a scheme has been adopted in this book, and separate sections are devoted to "gas evolution processes," in which a new gas phase is made to separate from a solid or liquid; "precipitation processes," in which a new solid phase is made to separate from a liquid; "solution and extraction processes," in which a new liquid phase is made to separate from a solid; and "partition processes," in which a new liquid phase is made to separate from a liquid phase.

Volumetric methods are those in which the amount of substance to be determined is estimated by measuring the volume of some reagent of known concentration, which must be used to completely transform the constituent being determined into some other form. The actual separation of a particular product is thereby avoided. Thus the silver can also be determined in the alloy by measuring the amount of sodium chloride solution of known strength which must be added to a solution containing a known weight of the alloy to precipitate all of the silver as chloride. Volumetric processes are conveniently classified with respect to the type of reaction upon which they are based; the three important classes are made the subject of separate sections of this book.

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Physico-chemical methods are those in which the unknown substance is determined by measuring some one of the various physical properties of a solution containing a known concentration of the sample under investigation, and comparing with the corresponding properties of solutions containing known concentrations of the substance to be determined. They are of rather restricted application, and are not strictly speaking chemical processes, but they are so frequently used by the analytical chemist that it is customary to group them with these.

Gas-analysis methods which are based upon the direct measurement of gas volumes form still a fourth group. They are used not only for the analysis of gaseous mixtures, but also for the determination of a large number of substances which yield gaseous products when submitted to the action of certain reagents. The successful use of these methods demands the employment of a large amount of specialized forms of apparatus; it has not been thought desirable to consider them in this book.

**The Training and Skill Required.** Success in quantitative work demands first of all a certain amount of dexterity in performing the mechanical operations involved. Training of the hand and eye, which results in the formation of habits of deftness and precision in manipulation is an essential prerequisite to work in this field. Certain individuals are able to acquire this skill with comparative ease, but, unfortunately, by far the great majority of persons can acquire it only through patient and persistent application. The beginner cannot be expected to do as rapid or as accurate work as the trained analyst, and only actual experience with a great variety of quantitative processes will teach the most effective methods of dealing with the problems which constantly arise in the execution of quantitative work and enable him to reduce to a minimum those errors of the process which depend upon manipulative skill.

**Theoretical Knowledge Necessary.** Although any person who has acquired the necessary manipulative skill may be able to execute the details of a carefully described quantitative process, his ability to make effective use of the process will be decidedly limited, owing to the fact that unforeseen contingencies, which his carefully worded description did not allow for, constantly arise.

It is only through a definite knowledge of the theory of each step of the process that the analyst can work intelligently and effectively; the mechanical performance of such operations without understanding the reason for each step is not worthy of being dignified by the term "quantitative analysis."

It should also be noted that the method employed must be adapted to the purpose for which the desired result is to be used. Frequently the rapidity with which a result can be obtained is of greater importance than extreme accuracy, and in such cases time and labor can be saved by neglecting certain of the details commonly used or by employing certain "short-cut" methods. Every quantitative determination is, therefore, a specific problem in itself, and an analysis of the various factors concerned in every detail of the proposed method may render it possible to increase either the accuracy of the work, or the productive capacity of the analyst. An accurate sense of proportion and judgment as to the importance and necessity of the details of quantitative work must be developed if the greatest efficiency is to be attained.

**The Literature of the Subject.** A vast amount of experimental work having for its object the development of new, or perfection of old, methods of analysis is being carried out continually. The results are published either in certain special journals devoted to this branch of chemistry, such as the *Zeitschrift für analytische Chemie* (Wiesbaden) and the *Analyst* (London) or in the more numerous chemical periodicals of a more general character. Especial importance should be attached to the reports of Committees and Associations, who coöperate in making tests of analytical methods under as nearly identical conditions as possible. Such, for instance, is the work of the Official Association of Agricultural Chemists or of the various Committees of the American Chemical Society. The progressive analyst will find it necessary to keep in touch with the newer developments of the subject, and even the beginner will derive much profit and inspiration from consulting the original sources of information upon which the methods he uses are based; hence, references to a limited number of important articles are added to some of the processes described in this book. Although a number of works which attempt to summarize all of the more important

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quantitative methods are available, more comprehensive and usually more up-to-date information can be found in the numerous manuals devoted to the elaboration of the methods which are especially adapted to the analysis of particular classes of materials, such as ores and metallurgical products, alloys, rocks, soils and fertilizers, foods, etc.

**Proposed Plan of Work.** The object of this book is to present the fundamental principles used in the general subject of quantitative analysis, and outline a method by which a working knowledge of the subject can be attained. In the plan of work here adopted the general features of each of the larger groups of quantitative processes is first discussed, then a limited number of typical illustrations of specific processes are described in detail and the various sources of error and further applications of the methods used suggested. A series of questions and problems designed to point out the reasons for certain features of the methods and emphasize the general principles used are appended to most of these descriptions. In the elaboration of each of the different classes of processes much matter of a more general character finds constant use; this has been presented in brief form in the series of chapters forming the first section of the book. Familiarity with all of the facts there presented is not an essential prerequisite to actual work with the methods described in the subsequent sections; all of it is necessary to a comprehensive knowledge of the principles of quantitative analysis, and these chapters should be carefully read and digested as progress is made in the practical part of the work.

**Strength of Reagents Used.** Many of the reagents used in quantitative analysis are prepared for the determination of one substance only and it is advantageous to make them of such strength that each cubic centimeter will react with an amount of that substance, which is expressed by a whole number of milligrams, such as one, five or ten. The methods of preparing such reagents will be given in the descriptions of the processes in which they are first used. Certain reagents, especially the acids and alkalies, are employed for a variety of purposes and are more conveniently used if their concentrations are made to bear a simple relation to normal. The term dilute as applied to these reagents will be used to designate

solutions which are approximately six-normal strength. The composition and methods of preparation of the acids and alkalies used as general reagents are given below.

Dilute or six-normal ammonium hydroxide is made by adding one volume of concentrated ammonium hydroxide (sp. gr. 0.9) to one and one-half of water. One cubic centimeter contains about 0.102 gram of ammonia.

Dilute or six-normal acetic acid is made by adding one volume of 80 per cent acid to one and four-tenths volumes of water. One cubic centimeter contains about 0.36 gram of acetic acid.

Concentrated or twelve-normal hydrochloric acid has a specific gravity of 1.19–1.2. One cubic centimeter contains about 0.44 gram of hydrochloric acid.

Dilute or six-normal hydrochloric acid is made by adding one volume of concentrated acid to one of water. Its specific gravity is 1.10 and 1 cc. contains about 0.22 gram of hydrochloric acid.

Concentrated or sixteen-normal nitric acid has a specific gravity of 1.42. One cubic centimeter contains about 0.99 gram of nitric acid.

Dilute or six-normal nitric acid is made by adding one volume of concentrated acid to one and six-tenths of water. Its specific gravity is 1.2 and 1 cc. contains about 0.38 gram nitric acid.

Concentrated or thirty-six normal sulfuric acid has a specific gravity of 1.84. One cubic centimeter contains about 1.77 grams of sulfuric acid.

Dilute or six-normal sulfuric acid is made by adding one volume of concentrated acid to five of water. Its specific gravity is 1.19 and 1 cc. contains about 0.29 gram of sulfuric acid.



## SECTION I

### GENERAL FEATURES OF GRAVIMETRIC PROCESSES

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## CHAPTER II

### THE DETERMINATION OF WEIGHTS

#### I. Theory of the Use of the Balance

**Construction.** Quantitative processes involve determinations of the relations existing between two masses of matter, but since both masses are determined by means of a beam balance under identical conditions the distinction between mass and weight can be disregarded. The accuracy of such processes must depend in part upon the accuracy with which the two weighings are made, and instrument makers have developed certain forms of balances known as "analytical balances" the use of which makes it possible to reduce the errors from this source to insignificant proportions. The details of the mechanism used by different makers for the adjustment and protection of such balances vary, but since all are based upon the use of essentially the same principles, only one type will be described here.

The beam of such a balance is represented in Fig. 1. It is constructed of such material, and in such a form, as to combine the maximum degree of rigidity and strength with the minimum weight. It is suspended at its center on a horizontal axis which is made of agate and accurately ground to a knife-blade edge, as shown at *A* of the figure. This axis rests upon a strip of polished agate supported upon the top of a pillar, and the beam is free to turn in a vertical plane about this axis. Two other knife-blade edges *B* and *B'*, which are of a similar construction, but with edges

turned upwards instead of downwards, are fixed at the two ends and are equidistant from the center. These edges sustain specially constructed stirrups, which are also provided with strips of agate, *C* and *C'* of the figure, at the points of contact; from them are suspended two pans, one of which supports the substance being

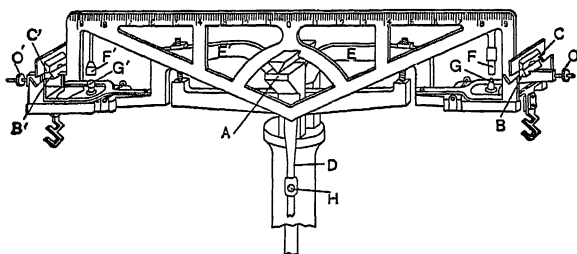


Fig. 1.—Beam of an analytical balance.

weighed, and the other the weights used. The beam may be regarded as a compound lever in which the fulcrum is at the axis of suspension. If the two arms are of equal length, and if the pans and the loads which they contain are of equal weight, the effect of the force of gravity upon the two ends of the beam is identical, and a depression of one end of the beam will produce a series of vibrations similar to those of a pendulum.

The process of weighing consists in placing the substance whose weight is to be determined in one pan, and adding weights to the other until the two counterbalance each other. This point can be recognized by observing the movements of the beam, and a pointer, the upper part of which is shown at *D*, is attached to it for the purpose of magnifying these movements; a small ivory scale, represented by Fig. 2, is placed just back of the end of the pointer, in order to make it possible to measure and record the magnitude of these movements with respect to the central axis. The center of this scale, which is directly below the axis of suspension, should be marked 10, the tenth division to the left zero, and the tenth to the right twenty; this method of marking the

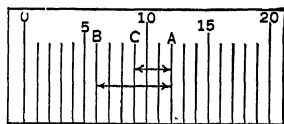


Fig. 2.—Scale of balance.

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scale at once indicates whether the numbers recorded are to the left or the right of the center.

As the movement of the beam is greatly retarded by friction, and as the friction losses increase very rapidly as the knife-blade edges lose their sharpness, it is necessary to protect these bearings against needless wear; hence, analytical balances are often provided with two sets of rests, known as "beam rests" and "pan rests" respectively. The beam rests are controlled by a milled button, placed at the center and on a level with the floor of the balance case. When rotated it turns an eccentric, which raises a rod passing through the center of the pillar of the balance, and this in turn raises two hinged arms  $E$  and  $E'$ , which lift the knife-blade edge  $A$  from the agate plate, and also the stirrups sustaining the pans from the knife-blade edges  $B$  and  $B'$  on which they rest. The hinged arms are also provided with two studs  $G$  and  $G'$ , which fit into a cup and a trough terminating the two studs  $F$  and  $F'$ , fastened to the beam. The effect of raising and lowering the beam rests is to bring the beam into exactly the same position with respect to the agate plate upon which it rests.

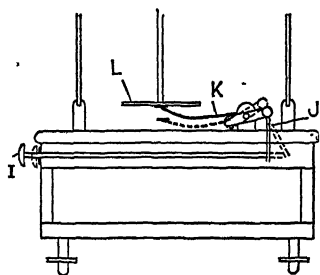


Fig. 3.—Base of balance case.

The pan rests are controlled by a small knob placed at the left of the center, as shown at  $I$  of Fig. 3. When a slight pressure is applied to this button, the rod to which it is attached moves the lever  $J$  which carries two arms  $K$  and  $K'$  and cause these to drop. Ordinarily these arms impinge upon the bottom of the pans  $L$  and  $L'$  and prevent needless vibration and wear of the bearings  $B$  and  $B'$ , but when they drop the beam is free to vibrate. As a protection against dust, moisture and air currents, the entire apparatus is enclosed in a glass case, one side of which consists of a movable glass slide.

**Conditions which Determine Accuracy.** An accurate comparison of the relative magnitudes of two masses cannot be made with such a balance unless certain essential conditions are complied with.

First, the point of suspension of the beam should be equidistant from the points of suspension of the two pans, for if these distances differ the loads sustained by the two arms act with unequal lever-ages. If the total length of the beam is known the difference in the lengths of the two arms can be calculated from the weights found to be necessary to counterbalance the same object, when placed first on one pan and then on the other. If we represent the length of the right arm by  $r$ , that of the left arm by  $l$ , the true weight of the object by  $W$ , the apparent weight when placed in the left pan by  $A$ , and when placed in the right pan by  $A + a$ , we have,

$$Ar = Wl, \text{ also } \check{W}r = (\underline{A} + a)l.$$

If we multiply these two equations together and simplify the resulting expression we can obtain the relation

$$(r)^2 : (l)^2 :: A + a : A.$$

It is also easy to show that the true weight of the object corresponds to the square root of the product of the two apparent weights, or since the two differ but slightly, it is represented with sufficient accuracy by the average of the apparent weights. Since it is not possible to make a balance whose two arms are absolutely equal, this method of "double weighing" is always used where extreme accuracy is demanded. The error which might result from this defect in the construction of the balance can usually be neglected if the same pan, usually the left-hand one, is used for all the weighings concerned in every determination made.

Second, the center of gravity of the entire system, that is, of the beam and the two loads which it sustains, must be slightly below the point of suspension of the beam. If the reverse relation holds, the system is in unstable equilibrium; if the two points fall together, the system is in neutral equilibrium, and vibration of the beam even with equal weights is impossible. If the center of gravity of the system is too far below the point of suspension, the deflection produced by a slight excess of weight in either pan is but slight, and the balance is not sufficiently sensitive. By means of a small weight, which slides up and down the pointer, but which can be fixed by means of a set screw (see  $H$  of Fig. 1), the center of gravity can be lowered or raised. If, however, this distance is

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made too small, the retarding effect of friction is relatively greater, and the movements of the beam are slow and uncertain.

Third, the point of suspension of the beam and of the two pans must be very nearly on the same horizontal line; otherwise, changes in the loads carried by the pans change the position of the center of gravity, and hence the sensitiveness. Since all balance beams yield slightly to heavy loads it is impossible to comply with this condition in all cases. Manufacturers usually endeavor to make  $A$  stand as much below the line joining  $B$  and  $B'$ , when the balance is empty as it stands above this line when the pans sustain the maximum permissible load; the balance should then show the minimum change in sensitiveness with an average load.

**Sensitiveness.** The sensitiveness of a balance is measured by the magnitude of the angle, corresponding to the change in the position of the pointer, produced by a slight excess of weight in either pan. Evidently this angle must increase as the length of the beam is increased, but it is undesirable to increase the length of the beam beyond a certain maximum, as the movements of the pointer then become correspondingly slow (and in this respect the behavior of the beam differs from that of a pendulum), and the time occupied in making a weighing is materially increased. The sensitiveness decreases as the weight of the beam and the other factors which produce friction increase. The third, and perhaps most important, factor is the adjustment of the center of gravity with respect to the point of suspension. The quantitative expression which represents the relation between these factors is given by the equation:

$$\tan \alpha = \frac{l \times w}{d \times q},$$

in which  $l$  is the length of the arm,  $w$  is the excess of weight in one pan,  $d$  is the distance referred to above and  $q$  is the weight of the beam. The correctness of this formula can be proven by making use of the principle of moments. Let  $AB$  of Fig. 4 represent the beam of a balance with equal loads in the two pans and  $A'B'$  the same balance with an additional 1 mg. weight in the right pan. The exact position of  $A'B'$  with respect to  $AB$ , which is measured by the angle  $\alpha$ , is determined by an equilibrium

between two forces, both of which act through the point  $O$ . One of these is exerted by the 1-mg. weight ( $w$ ) acting in the direction of the force of gravity, with a leverage corresponding to the perpendicular distance between  $B'$  and  $L$ , that is to  $B'L$ . The other is exerted by the weight of the beam  $q$ , not including the pans, acting in the same direction with a leverage corresponding to the perpendicular distance between  $S$ , which is the center of gravity of  $q$ , when the beam is at  $A'B'$ , and the

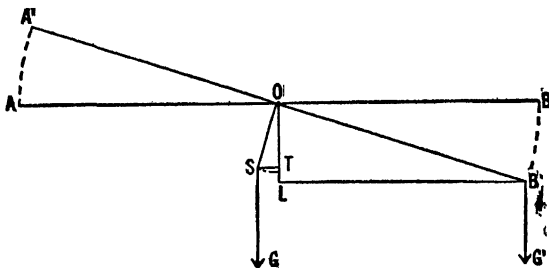


Fig. 4.—Diagram representing theory of the balance.

line  $OL$ , that is  $ST$ . Since the two effects counterbalance each other we have

$$w \times \text{distance } B'L = q \times \text{distance } ST.$$

If we represent  $OB$  by  $l$ ,  $B'L = l \cos \alpha$ ; if we represent  $OS$ , the distance between the point of suspension of the beam and the center of gravity of  $q$  with the beam at either  $AB$  or  $A'B'$ , by  $d$ , then  $ST = d \sin \alpha$ . Hence,

$$w \times l \times \cos \alpha = q \times d \times \sin \alpha$$

and therefore

$$\frac{\sin \alpha}{\cos \alpha} = \tan \alpha = \frac{w \times l}{q \times d}$$

As ordinarily used the sensitiveness represents the number of scale divisions through which the pointer is deflected by 1 mg. Although it is desirable to make the sensitiveness large by reducing the value of  $d$ , it cannot be reduced below a certain limit, which depends largely upon the skill used in the construction of the



reached are designated by the letters of the alphabet. The true point of rest  $C$  can be found by either of the following formulae:

$$C = \left( \frac{a + c + e + g}{4} + \frac{b + d + f}{3} \right) \div 2, \quad (1)$$

$$C = \left( \frac{b + d + f}{3} + \frac{c + e}{2} \right) \div 2. \quad (2)$$

**The Accurate Method of Weighing.** Having determined in the manner described the point of rest of the empty balance, the weight of any substance can be determined by placing it on one pan of the balance, and adding weights to the other until the point of rest corresponds to that originally found. If accurately carried out the process is a slow one, and may be abbreviated by an equally exact inter-

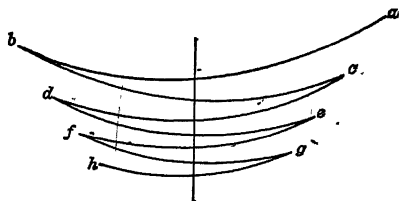


Fig. 5.—Diagram representing movement of pointer.

polation process, which depends upon the fact that the change in the point of rest is directly proportional to the weight by which that change is produced. In using this method the unknown substance is placed on the left pan and weights added (not using fractions of milligrams), until the point of rest is not far from that of the empty balance. If this point of rest is to the right of  $C$  another milligram is added to the weights in the pan, and the point of rest again determined, or if it is to the left, 1 mg. is removed and the point of rest determined. The difference  $A - B$ , in which  $A$  and  $B$  represent the points of rest corresponding to the lesser and the greater weights respectively, gives the deflection produced by 1 mg. In order to change the point of rest to that of the empty balance  $(A - C) \div (A - B)$  mg. must be added to the lesser weight. The interpolation method is represented graphically in Fig. 2, which shows the actual positions of  $A$ ,  $B$  and  $C$ , on the ivory scale in a specific case. It is obvious that  $(12 - 9) \div (12 - 6)$  or 0.5 mg. must be added to the weight which gave the point of rest  $A$  in order to



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counterbalance the unknown substance in the left pan. The value of  $(A - B)$  is approximately constant, and unless there are wide variations in the load sustained by the beam, may be assumed to be exactly so, hence, it is often possible to omit the determination of either  $A$  or  $B$  if the proper constant has been previously determined. The value of  $C$  does not usually change much during the course of a laboratory period, and need only be determined once. This method of weighing is the most accurate in use and with experience is rapidly executed. Under favorable conditions it should be possible to reduce the error involved in weighing by this process to one-tenth of a milligram, but this represents the extreme limit of accuracy which can be attained with the ordinary analytical balance. If a greater degree of accuracy is demanded a more carefully constructed "assay balance" must be used, but this should not be employed for weights which exceed 5 grams.

**Abbreviations of Accurate Method.** In all kinds of quantitative work it is the percentage rather than the absolute error which has to be considered, and where large amounts of material are to be weighed the above method may be shortened. If we are to weigh a precipitate of about the magnitude of 1 gram, and weigh to within one-tenth of a milligram, the percentage error involved will be one-hundredth, which is insignificant, as compared with the other unavoidable errors of most quantitative processes, and even if the error involved is a half milligram the percentage error is not excessive. If, however, our precipitate weighs two-tenths of a gram an absolute error of a half milligram cannot be safely disregarded. The abbreviation referred to above consists in making a rough mental calculation of the point of rest from a mere inspection of the movement of the pointer. It may be further noted that most of the weighings made actually involve the difference between two weights, namely, the weight of the empty vessel and that of the vessel and substance. If the same point of rest is assumed for both weighings, the same error will appear in both and the difference will give the correct value of the magnitude desired. The point usually assumed is the center of the scale. Hence the process of weighing which may be used in such cases consists in manipulating the weights till the pointer swings to

approximately an equal number of divisions on both sides of the center of the scale, making the proper allowance for the decrement in the amplitude of each vibration. The error involved in this method should not exceed three-tenths of a milligram. Some judgment must be used as to which of these methods of weighing should be employed, but a fairly satisfactory general rule is to use the more accurate method when the quantity weighed is less than three-tenths of a gram.

**The Weights Used.** Since the results of quantitative processes are usually expressed in terms of the ratio of the substance found to the substance used, and since the same set of weights is used to determine the value of both of these magnitudes, the absolute value of the standard or unit mass employed is of no significance. If the weights used are consistent between themselves, that is, if the different pieces bear to each other the exact relation for which they are used, no error will appear in the final result. If, however, as in the assay of gold and silver ores, the result is to be reported in terms of the money value per ton, the absolute value of the unit of weight employed is of the greatest importance. The sets of weights sold by firms of established reputation are frequently sufficiently accurate for most kinds of work, but the results obtained with them will always be subject to some uncertainty until they have been accurately tested. Such weights should be handled with ivory-tipped pincers and kept in a closed box when not in use. Platinum weights should not change in value even after years of constant use, but aluminum weights are subject to slight corrosion and must be more carefully protected.

The manipulation of very small weights, especially those below 5 mg. in value, is troublesome and is usually avoided by the use of a "rider." This is a piece of platinum or aluminum wire bent in such form as to hang on the beam of the balance, and is easily moved from place to place on the beam by means of a hook. If such a rider, whose weight is exactly 5 mg., is placed on the beam of the balance exactly above the point of suspension of the pan containing the weights it would have the same effect as the addition of 5 mg. to that pan, or if placed in any position between this point and the point of suspension of the beam it

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would have an effect proportional to its distance from the point of suspension of the beam. If the beam is divided into five equal parts each division would be equivalent to 1 mg. Further subdivision of these large divisions enables one to add tenths of a milligram as desired.

**The Calibration of Weights.** It is often necessary to calibrate accurately a set of weights. This involves first a determination of the exact relations between the different pieces composing the set, and second a reduction of the values thus obtained to the absolute metric unit or some other convenient standard. The method can be readily illustrated by a concrete example. In this work the 5 mg. weight was temporarily adopted as a standard of reference and was found to agree absolutely with the rider of the balance. By comparing systematically the different pieces of the set on an assay balance the results recorded in the accompanying table were obtained. In this table the first column represents the marks on the weight placed in the left pan of the balance, the second column the weights added to the right pan, and the third the position of the rider on the beam of the balance.

5	0	5	5	5
10	5	5	10	10
10*	10	0	10	10
20	10+10*	0	20	20
50	20+10+10*+5	5.08	50.08	50
100	50+20+10+10*+5	5.08	100.16	100
100*	100	0.05	100.21	100.1
200	100+100*	0.05	200.42	200.2
500	200+100+100*+50+20+10+10*+5	5.08	500.95	500.3
1000	500+200+100+100*+50+20+10+10*+5	5.12	1001.94	1000.7

The figures in the fourth column represent a summation of those in the second and third plus the corrections previously found, and hence the values of the different weights in terms of the 5-mg. weight.

The 1-gram weight was next compared with a standard metric gram on an assay balance and found to have the value 1.00075. Multiplying the series of figures in the fourth column by the

factor ( $1.00075 \div 1.0019$ ), that is 0.9988, reduced them to the corresponding values in terms of absolute metric units and gave the results which appear in the last column of the table. The figures which appear in the second decimal place have no significance in most analytical work and should be neglected.

**Correction for Buoyancy.** The apparent effect of gravity upon any object which is surrounded by the atmosphere is less than the true effect by an amount corresponding to the weight of the volume of air which it displaces. If the loads suspended by the two pans of the balance displace the same volume of air buoyancy affects both equally, but if the substance being weighed and the weights used to counterbalance it differ in volume buoyancy affects the load displacing the greater volume to a greater degree than the other, and causes a corresponding error. The magnitude of this error can be calculated from the weight of a unit volume of air and the densities of the substance weighed and the weights used. The method of making the calculation can be expressed by means of the formula:

$$W = A + A\left(\frac{1}{D_s} - \frac{1}{D_w}\right)D_a,$$

in which  $W$  and  $A$  are the corrected and apparent weights respectively in grams,  $D_s$ ,  $D_w$  and  $D_a$  are the density in grams per cc. of the substance weighed, the weights used and the atmosphere respectively. The value of  $D_a$  varies with varying temperature and pressure, but the total effect upon the final result due to these changes is negligibly small. The expression  $\left(\frac{1}{D_s} - \frac{1}{D_w}\right)D_a$  is a

constant for all weighings of the same substance and if a number of weighings of the same kind of substance are being made time can be saved by evaluating this part of the formula separately.

**The Error Resulting from Hygroscopic Water.** Any solid object which has not been especially dried and maintained in an atmosphere which is free from water vapor retains a film of hygroscopic water upon its surface. If the surface presented is large, the true weight of such an object may differ from the apparent weight, that is the weight determined under ordinary atmos-

pheric conditions, by several milligrams; and further, the difference varies with the amount of water in the atmosphere. Although this film of water can be expelled by heating the object to 100° C. for a few minutes it is not readily possible to entirely prevent the reabsorption of hygroscopic water while it is being cooled and weighed. A 15-gram crucible, for example, which has been allowed to cool in a desiccator and which is weighed in a balance, the case of which contains a jar of calcium chloride, will frequently show a gain of from one to three-tenths of a milligram on long standing on the balance pan. When it is necessary to weigh accurately to one-tenth of a milligram this becomes one of the most troublesome difficulties to avoid.

Since most weighings are made in some form of a container, such as a crucible or bottle, the weight actually used in the final calculation represents the difference between the weight of the container plus substance and the container, and the error resulting from the absorption of hygroscopic water can often be reduced to negligible proportions by submitting both to exactly the same conditions before weighing. If, for example, the empty crucible and the crucible plus the substance to be weighed are ignited, placed in a desiccator while still warm, allowed to stand for an hour and then weighed at once the amount of hygroscopic water absorbed by the crucible in the two cases is practically the same, but not exactly so unless the percentage of water vapor in the atmosphere has remained constant. The only error to be considered in such a case is that due to the absorption of water by the substance itself, which can usually be neglected unless it is decidedly hygroscopic. If it is decidedly hygroscopic, it becomes necessary to use a closed container. When the container cannot be heated to a temperature necessary to drive off all hygroscopic water, wiping with a dry cloth has to be substituted. If the surface presented by the container is very large, variations in the moisture content of the air may lead to errors which cannot be neglected. In such cases it is desirable to prepare a counterpoise of about the same surface area as the vessel to be weighed, to submit both vessels to the same treatment before both weighings and to substitute the counterpoise for some of the weights employed in both cases. It may be assumed that variations in the atmos-

pheric conditions will affect the amount of water retained by the two vessels to the same extent, and that no error from this source will appear in the difference finally found.

## II. Rules for the Use of the Balance

Although the general facts and principles upon which the use of the balance is based have been presented in the preceding section, there are a number of details of a purely practical nature which must be observed if the balance is to be maintained in good working order. These are elaborated in the form of the series of rules given below.

First, in order to prevent wear of the bearings, and consequent rapid decrease in the sensitiveness of the balance, large weights should never be placed on or removed from the balance pans, unless the beam- and pan-rests are in position; if the weight being added or removed does not exceed 100 mg. the pan-rests alone will suffice. Both rests should always be left in position before leaving the balance.

Second, the floor of the balance case and the pans should be kept perfectly clean. If substances are spilled within the case they should be brushed up at once with a fine brush or cloth.

Third, no solid substances except certain metals and alloys should be placed in contact with the balance pans. No liquids of any description should be brought into the balance case unless retained in tightly stoppered bottles.

Fourth, hot objects should be allowed to cool to a temperature not greatly in excess of the normal temperature of the balance room before being weighed. If this precaution is not taken disturbing air currents are set up within the balance case. For a like reason the slide of the balance case should be kept closed while the movements of the beam are being observed.

Fifth, the weights should always be handled with bone-tipped forceps and should be carefully protected from dust and fumes.

Sixth, if the point of rest of the empty balance differs from ten by more than two units, or if the balance fails to behave properly, ask the instructor in charge to make whatever adjustments may be necessary.

### **III. Details of Procedure for the Determination of Point of Rest**

Seat yourself squarely in front of the balance case so that your line of vision is directly opposite the center of the balance. Release the beam-rests by turning the button at the center of the case, then the pan-rests by pressing the small knob to the left, next gently lower the rider till it rests on the end of the beam and allow it to remain just long enough to displace the pointer about ten divisions on the ivory scale, and finally remove the rider and permit the beam to swing freely. Take an odd number of consecutive readings (five are sufficient) corresponding to the extreme positions reached by the pointer. Add together the averages of the two sets of readings, one set representing all the readings taken on the right of the center, the other all the readings taken on the left of the center, and divide the sum by two. This gives the point of rest of the empty balance. Repeat the determinations till results are obtained whose extreme differences do not exceed ~~two-tenths of a division~~.

### **IV. Details of Procedure for the Determination of the Weight of a Watch Glass**

**Elaborate Method.** Hold a clean watch glass over a gauze heated by the flame of a burner until it is decidedly hot to the touch, then place on a clean support inside a desiccator, and allow to cool for twenty minutes. Transfer the glass by means of clean dry pincers to the left pan of the balance and add in regular succession weights of decreasing value to the right pan until the correct weight is determined to within 10 mg., if the balance is provided with a 10-mg. rider, and to within 5 mg., if it is provided with a 5-mg. rider. Next, vary the position of the rider on the right arm, placing it at points corresponding to entire milligrams, until the weight is found to within one mg. Finally determine accurately the point of rest, first, with the rider in the position which makes the total weights used slightly less, and second in the position which makes the total weights used slightly greater than that of the watch glass. These relations can

be determined by noting whether the pointer swings decidedly to the right or the left as the changes are made.

Let  $A$  represent the point of rest found with the lesser weight,  $B$  that found with the greater weight, and  $C$  the point of rest of the empty balance. Calculate the correction, expressed in milligrams, to be added to the lesser weight necessary to shift the point of rest from  $A$  to  $C$  by dividing  $(A - C)$  by  $(A - B)$ , and add this correction to the lesser weight.

Verify the accuracy of the result by adding, by means of the rider, the fraction of a milligram calculated to be necessary and again determine the point of rest. If the work has been accurately carried out, and if the balance is properly constructed and adjusted, the points of rest obtained should not differ from that of the empty balance by more than two-tenths of a division of the ivory scale.

Make a permanent record of the weight thus obtained in the laboratory notebook, in which all weighings and the data upon which they are based should be recorded when obtained. Disregard all figures beyond the fourth decimal place.

**Abbreviation of the Method Outlined.** In subsequent work this method of weighing may often be abbreviated. Where the weight actually determined is the difference between the weight of the containing vessel and the weight of that vessel plus another substance, the point of rest of the empty balance may be assumed to be ten. Where the magnitude of the mass weighed is not less than 0.25 gram the accurate determination of the points of rest may be omitted and the weight determined with sufficient accuracy by changing the position of the rider on the beam until the pointer swings to approximately the same distance on either side of the point of rest of the empty balance, making a slight allowance for the decrease in the value of each successive vibration,

## V. Details of Procedure for the Calibration of a Set of Weights

Determine the relations between the different pieces composing the set, using the procedure outlined on page 18. It is not necessary to reduce the results to the absolute metric standard.



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### VI. Questions and Problems. Series 1.

1. Calculate the true weight of a crucible from the following data: point of rest of empty balance, 10.8; point of rest with crucible on left pan and 8.7421 grams on the right pan, 10.2; point of rest with crucible on left pan and 8.7434 grams on right, 8.1. *Ans.* 8.7417 grams.

2. The right arm of a balance is divided into five equal divisions. If a rider, which weighs 4.85 mg. is placed at the point on the right arm corresponding to 3.7 divisions, what weight placed on the left pan would exactly counterbalance it? *Ans.* 3.59 mg.

3. The right arm of a balance has a length of 76 mm., the left arm of 75.96 mm.; the apparent weight of a crucible placed on the left pan is 10.0421 grams. What is the correct weight of the crucible? *Ans.* 10.0474 grams.

4. What error would result in weighing a precipitate whose true weight is 0.4210 gram, in the crucible referred to above, if (a) both empty crucible and crucible plus precipitate are weighed in the left pan, (b) if the crucible is weighed on the left pan and the crucible plus precipitate in the right pan?

*Ans.* (a) -0.0002 gram, (b) 0.0108 gram.

5. The total length of the beam of a balance is 154 mm., the weight is 33.5 grams, and the length of the pointer is 234 mm. If it is desired so to adjust the balance that 1 mg. will deflect the end of the pointer through 2 mm., what must be the difference between the point of suspension and the center of gravity of the beam and pans? *Ans.* 0.27 mm.

6. In calibrating a set of weights it is found that if the weight marked 10 mg. is assumed to weigh exactly 10 mg. the weight marked 5 grams must weigh 5.0120 grams. If the actual weight of the former is 9.9 mg. what is the true weight of the latter? *Ans.* 4.9619 grams.

7. What percentage error results from failure to correct for buoyancy of the air in weighing a sample of gypsum, assuming that the density of the brass weight used is 8.33 grams per cc., that of the gypsum is 2.32 grams per cc., and that of air under the prevailing conditions is 1.2 grams per liter? How would the error be affected if (a) platinum weights were used? (b) quartz weights were used? (c) if the air was completely instead of partially saturated with water vapor? (d) the sample were weighed in a platinum rather than a glass container? *Ans.* 0.04.

## CHAPTER III

### THE GENERAL OPERATIONS OF QUANTITATIVE PROCEDURE

#### I. Preparation of the Substance for Analysis

**Theory of Sampling.** The amount of substance actually employed in making a quantitative analysis is comparatively small, and the result obtained is of but little value unless the portion actually used accurately represents the average composition of the entire mixture. In the analysis of gases and liquids homogeneous mixtures are very easily obtained by a slight amount of stirring, but in the analysis of solid mixtures it is usually necessary to prepare a "sample." The difficulties which arise in preparing a representative sample of a solid mixture result from differences in size and lack of uniformity in the distribution of the different constituents, and from differences in the hardness and the specific gravity of these constituents. The general method of procedure in sampling a non-homogeneous solid, whether it represents a carload or a few pounds is essentially the same. It involves removing and setting aside, according to a uniform plan, a fractional part of the total amount, reducing the portion set aside to a finer state of division, mixing thoroughly, and repeating this cycle of operations until a sample of such fineness is obtained that the small amount actually weighed out represents the entire original mass. The fundamental principle which must be kept in mind is that the fineness to which the sample is crushed at each cycle must be such that the ratio between the size of the sample and the size of the largest particle is sufficiently large. The size of the largest particle must be so small that the addition of one such particle to the portion which has been selected does not

change the average composition of the mixture by an appreciable amount.

**Calculation of the Maximum Size of Particle.** The maximum size of particle which is permissible depends upon a number of factors, and can be calculated if certain assumptions are made. The method is most conveniently outlined by the consideration of a specific case.

Let it be assumed that a lump of iron ore, which weighs 1000 grams, consists of 200 grams of quartz, which has a specific gravity of 2.5 and contains no iron, and 800 grams of hematite, which has a specific gravity of 4.5 and contains 60 per cent of iron. Let it be assumed further that it is desired to crush this lump to such a degree of fineness that when one-fourth of the well-mixed mass is selected the addition of a further particle of quartz will not reduce the percentage of iron, or of a further particle of hematite will not increase the percentage of iron, by more than one-tenth of one per cent. The correct percentage of iron in the lump is evidently 48, and if  $x$  and  $x'$  represent the respective weights of quartz and hematite whose size is just sufficient to meet the requirements named, the following expressions are true.

$$48 - \frac{(250 \times 48) + (x \times 0)}{250 + x} = 0.1,$$

$$\frac{(250 \times 48) + (x' \times 60)}{250 + x'} - 48 = 0.1.$$

When these expressions are solved  $x$  will be found to have the value 0.52 gram, and  $x'$  2.1 grams. The volume of a quartz particle which weighs 0.52 gram is evidently 0.208 cc. and if it is assumed to have the form of a perfect cube its length would be approximately 0.6 cm. The volume of a hematite particle which weighs 2.1 grams is evidently 0.46 cc. and if it is also assumed to be a cube, its length would be 0.77 cm. Hence the sample should be crushed fine enough to pass through a sieve which has openings not exceeding 0.6 cm. in diameter and since the assumptions

here made are not actually realized, a sieve with still smaller openings should be used if the specified degree of accuracy in the preparation of the sample is to be assured.

**Methods of Selection.** The simplest method of selecting a fractional part of the mixture is to turn over the entire mass with a shovel or spoon, and set aside every tenth, fifth, or second shovel or spoonful. Another method is to distribute the entire mass in the form of a cone-shaped pile, flatten the pile slightly, and remove a sector representing one-quarter or one-half of the pile; it can be assumed that the large and small particles and the light and heavy particles are distributed symmetrically with respect to the central axis of such a cone. A large number of mechanical devices, which automatically separate a fractional part of all the material passed through them, are used where the sample is large.

**Methods of Powdering.** A great variety of grinding or shredding machines, which are especially adapted to the nature of different classes of materials, are in use. Although the grinding parts of such machines are made of hardened steel, appreciable amounts of iron are added to the sample during the grinding process if the sample contains constituents whose hardness approaches that of steel. This is usually neglected in commercial work, but cannot be tolerated in many lines of scientific work. In such cases the sample must be pulverized by hand by means of a mortar and pestle which are made of agate. It is sometimes advantageous to separate out the coarse from the fine particles during the grinding process; but since certain constituents of the mixture may be more easily reduced than others, none of the sample can be rejected, that is, the entire sample must be made to pass through the sieve used.

**Methods of Mixing.** Mixing is best performed by placing the mass in a cylindrical vessel, which is then carefully corked and rotated by means of a motor. The same result can be obtained more slowly by hand rotation. Another method consists in placing the sample on a large piece of rubber "sampling-cloth" and rolling the contents toward the center by raising successively the opposite corners of the cloth. Mixing and grinding can be effected simultaneously by means of the small "ball mill" represented

in Fig. 6. It consists of a porcelain jar, which contains in addition to the sample a large number of porcelain balls. When closed and rotated either by hand or by the use of a motor, these balls rapidly reduce the sample to a fine homogeneous mixture.

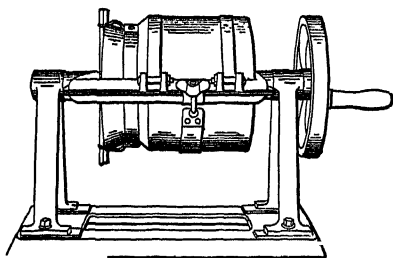


Fig. 6.—Ball mill.

percentage is large the fine particles tend to stick together and may make it impossible to powder and mix the sample properly. Frequently a mass which seems to be dry becomes moist and sticky as soon as it is powdered, owing to water or solution held within the interior of the larger masses.

The chemist is usually expected to report results on the basis of the mixture actually received. If he dries the mixture submitted to him in order to make it possible to prepare a representative sample the results obtained will not represent the composition of the original mixture. In such cases it becomes necessary to save out a sufficient amount of the original mixture to permit of an accurate determination of the water present, and to multiply the results of the analysis by the difference between 100 and the percentage of water found in order to report the percentages present in the original mixture.

If the sample contains a small amount of hygroscopic water only, it is preferable not to dry it, for, since all finely divided substances are at least appreciably hygroscopic, it is often difficult to preserve such samples and to weigh them out accurately.

**Methods of Drying.** Hygroscopic water is usually determined by drying the sample in an oven, similar to the one shown on page 32, which is kept at a temperature of  $105^{\circ}\text{C}$ . This method cannot be used if the sample loses chemically combined water, or undergoes other changes at this temperature. In such cases dehydration is best effected by placing the sample in a "desiccator," one form of which is represented in Fig. 7. It consists

of a glass box provided with a tightly fitting cover and containing some substance, such as concentrated sulfuric acid or calcium chloride, which is a good absorbent of water. Its effectiveness depends upon the equilibrium between the dehydrating agent and the water vapor in the air of the desiccator. This equilibrium will be discussed in Chapter VI. The rate of dehydration in such a device is usually low, and days or even weeks may be necessary to reduce the moisture content to a minimum value which can be attained with the dehydrating agent used.

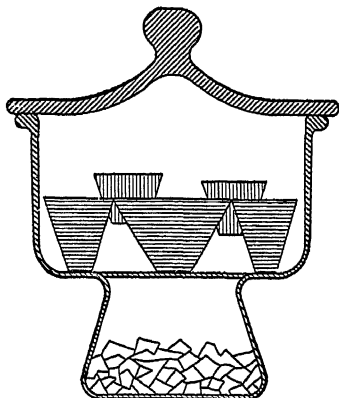


Fig. 7.—Desiccator.

Finely divided substances which have been separated from solutions sometimes require special treatment before they are properly prepared for analysis. The liquid associated with the solid can be reduced to a small percentage by use of the mechanical filtering devices described on page 149, and to still smaller percentages by absorbing the solution by means of filter paper or a plate of porous porcelain. The finely powdered solid is repeatedly pressed with a spatula against fresh portions of the absorbing medium. By capillary action these media gradually take up most of the adhering water and make it possible to obtain a homogeneous sample in which the water can be actually determined. However, if the composition of the soluble components of the solution differs considerably from that of the solid this procedure may not give the true composition of the solid. In such cases the solution should be eliminated by washing with some easily volatile liquid which does not dissolve the solid appreciably. Successive treatments with small amounts of mixtures of alcohol and water, gradually increasing the percentage of alcohol, often serve to accomplish this purpose.

## II. Methods of Producing and Applying Heat

**Sources of Heat Used.** Many quantitative operations depend for their success upon the maintenance of definite temperatures for either long or short time intervals. The range of temperatures used is wide, and a great number of devices become desirable or necessary if efficiency and speed are to be attained. Although it costs less under normal conditions to produce heat by the consumption of gas than of electricity, electric heaters are more easily controlled, and frequently the difference in cost is more than offset by the greater certainty of operation and the absence of undesirable gaseous combustion products.

**Heating with an Electric Current.** The amount of heat produced by the passage of a current through a resistor varies with the product of the resistance offered and the square of the current transmitted, and, therefore, depends upon the current strength to a greater extent than the resistance. Various materials are used as resistors in constructing devices for this purpose; the most convenient are certain alloys, such as German silver, monel metal, and nichrome, which possess a high specific resistance, a high melting point, and ability to resist oxidation at high temperatures. The alloy last named possesses all of these properties to a maximum degree and can be obtained at small cost in the form of wire or ribbon of any desired size.

In constructing an electric heating device the factors of greatest importance are the voltage of the current available, which may be either direct or alternating; the masses and specific heats of the substances used in its construction; the heat losses from radiation and conduction; and the temperature which it is desired to attain. If the voltage is fixed, the length and size of the wire used as a resistor are the essential features to be decided on, and, owing to the large number of variables concerned, these must be determined by experiment rather than by calculation. It may be noted, however, that a long piece of coarse wire forms a more durable resistor than a short piece of fine wire of equal resistance. The temperature attained with such devices is fairly constant so long as the voltage and current and the heat loss are constant. The temperature can be reduced by reducing the current, and is therefore easily

regulated by introducing a rheostat in the circuit in series with the resistance wire.

**Devices Used for Evaporation.** The evaporation of solutions rarely necessitates the use of temperatures greatly in excess of  $100^{\circ}\text{C}$ . Temperatures somewhat below this point, but sufficient for the evaporation of most aqueous solutions, are conveniently attained by the use of a "steam bath," that is, a vessel in which water is made to boil vigorously, either by a coil of steam pipes or by the flame of a gas burner, and which has a cover provided with openings for the reception of the vessels containing the solutions to be evaporated. A bath of sufficient size to accommodate a large number of such vessels is an essential part of the equipment of a quantitative laboratory. It has the great advantage of keeping the solutions at a uniform temperature well below the point at which mechanical losses are to be anticipated.

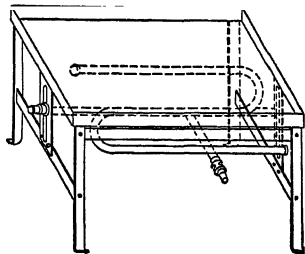


Fig. 8.—Sand bath.

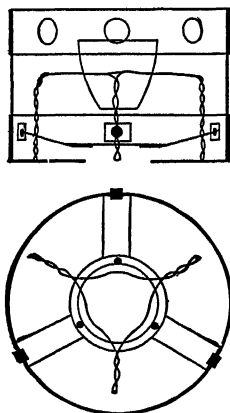


Fig. 9.—Asbestos muffle.

Direct heating of the vessel containing the solution by a flame is usually avoided by interposing a plate of metal, forming a "hot-plate," or a tray filled with sand, forming a "sand bath," between the flame and the vessel. A sand bath of this character is represented in Fig. 8. It gives a higher temperature, and therefore more rapid evaporation than the steam bath, and the temperature can be controlled by varying the gas supplied to the burner or the thickness of the layer of sand used. It is especially useful where the liquid is retained in a flask and gentle ebullition is not objectionable.

When it becomes necessary to attain still higher temperatures, as in the evaporation of sulfuric acid, the vessel containing the substance to be evaporated may be placed inside a "muffle,"



that is, an outer shell which protects the inner vessel from the flame and permits it to be heated by radiation only. A large nickel or iron crucible can be used as a muffle for this purpose, but the device represented in Fig. 9, which is made of heavy asbestos board and bound with sheet iron, is more durable.

**Devices for Drying Solids.** The amount of vapor to be expelled in drying solids is usually small, as compared with that expelled

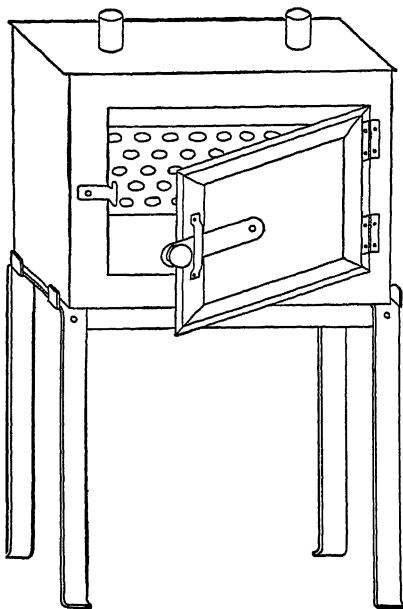


FIG. 10.—Air bath.

in evaporating liquids, and the apparatus used may take the form of a rectangular oven, such as is represented in Fig. 10. Its temperature can be roughly regulated by varying the height of the flame or the size of the burner by which it is heated; if greater refinement is necessary an automatic gas-regulator, which increases or decreases the gas supply as the temperature falls below or exceeds that for which the regulator is set, can be used. Ovens of larger size, which are used for cooking and can be obtained from hardware dealers, can often be used to advantage.

Still another device, represented in Fig. 11, consists of a double-walled oven, in which the intervening space is filled with a liquid whose boiling point is slightly above the temperature desired. This liquid is kept at the boiling point by means of a burner, and the vaporized liquid is condensed and returned to the oven as fast as produced. The liquids most frequently used are water, which gives a temperature in the oven of about  $96^{\circ}\text{C.}$ , and toluene, which gives a temperature of nearly  $105^{\circ}\text{C.}$  In all devices of the oven type the water vapor which is generated escapes but

slowly and their efficiency, that is, the rate at which drying is affected, is not great. A further objection to ovens heated by gas is that some of the combustion products may enter the oven and produce objectionable effects upon the substance being dried. For this reason the electrically heated ovens, which can now be purchased from dealers in chemical apparatus, are to be preferred to all others, even though their cost is somewhat large.

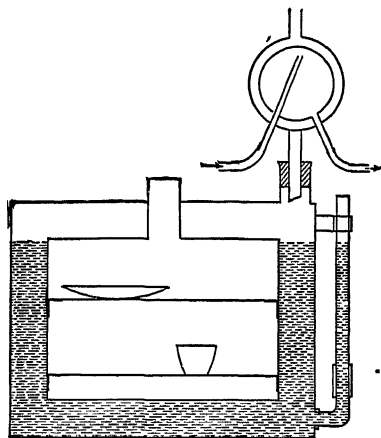


Fig. 11.—Constant-temperature oven.

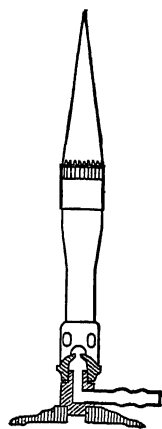


Fig. 12.—Méker burner.

**Temperatures Attainable by the Use of Gas Burners.** Direct heating of the substance in a crucible is always to be preferred where there is no danger of exceeding the maximum permissible temperature. The temperature actually attained inside of the crucible depends upon the type of burner used, the calorific value of the gas burned, and the masses and specific heats of the substances heated, that is, the crucible used, the triangle used to support it, and the substance which it contains.

The Bunsen burner is decidedly inferior to the more recently devised Méker burner, a vertical projection of which is represented in Fig. 12. In the former the air supplied at the base is not sufficient for the gas burned and a long cone-shaped flame results; the area over which active combustion takes place is comparatively large, and the highest temperature is attained at

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the apex of the inner blue cone. In the Méker burner the air supplied at the base is sufficient, but "striking back" is prevented by the grid and enlargement at the outlet; the entire combustion takes place within a few millimeters of the top of the grid, and the heating effect is therefore concentrated in a single horizontal plane.

The temperatures actually attained in the interior of uncovered crucibles of different sizes and materials, which were heated on triangles of nichrome wire by the two forms of burners are given in the following table:

Crucible Heated	Berlin Porcelain 00	Berlin Porcelain 0	Berlin Porcelain 1	Platinum	
Capacity.....	10 cc.	15 cc.	23 cc.	14 cc.	29 cc.
Temperature with Bunsen burner.....	820° C.	780° C.	780° C.	840° C.	780° C.
Temperature with Méker burner.....	880° C.	840° C.	770° C.	890° C.	805° C.

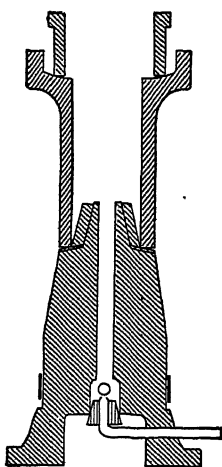


Fig. 13.—Chaddock burner.

Somewhat higher temperatures are attained by using covers on the crucibles, but this prevents the circulation of air within the crucible and the escape of gases which may be liberated by the substance heated in the crucible, both of which effects are undesirable.

Still higher and more uniform temperatures can be reached by surrounding the burner and crucible with a shield, which cuts off air-currents and greatly reduces the radiation losses. This device is utilized in the burner devised by Chaddock, a vertical projection of which is shown in Fig. 13. Combustion of the gas used is effected exactly as in the Bunsen burner, but the entire burner is made of porcelain, and a fire-clay chimney,

which fits upon it loosely, both reduces the losses from radiation and forms a support for a triangle over which a crucible can be heated.

Where still higher temperatures are needed a "blast lamp," that is, a burner which is supplied with a blast of air, or an electric furnace can be used. An effective blast lamp is capable of producing a temperature of  $1100^{\circ}$  C. in a platinum crucible of moderate size.

**Construction of an Electric Furnace.** Small electric furnaces designed to heat crucibles of moderate size are extremely advantageous. The plan of an inexpensive and easily constructed furnace is represented in vertical and horizontal projection in Fig. 14. The heating unit consists of an alundum core *A*, 2 inches in diameter, around which is wound 15 feet of No. 23 nichrome wire coiled in the form of a helix 4 feet long and one-eighth of an inch in diameter. The core and helix rest upon a piece of asbestos board supported by a ring of porcelain *B*; it is placed in the center of a cylinder of sheet copper some 4 inches in diameter, which is supported in a vertical position by means of a wooden base *C*; but is insulated from the base by strips of thick asbestos. The entire space between the core and cylinder is filled with a compact mass of asbestos. The ends of the helix are brought through but insulated from the copper cylinder and are attached to binding posts screwed into the base.

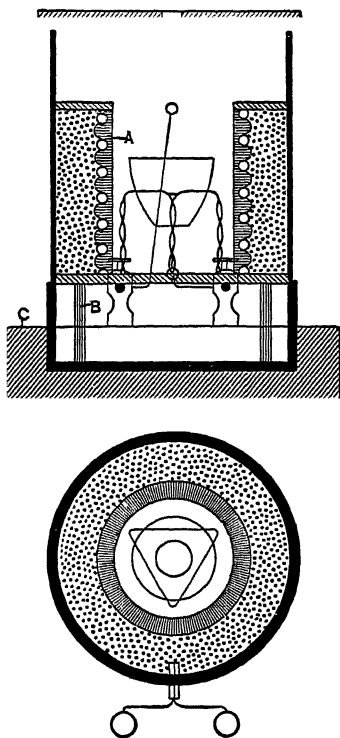


Fig. 14.—Plan of an electric furnace.

When this furnace is attached to a 110-volt circuit it consumes

about 3 amperes of current. When a crucible is placed inside the core and the furnace is covered, the temperature inside the crucible rapidly rises to  $1000^{\circ}\text{C}$ . A lower temperature can be attained by placing a rheostat in series with the heater, but it is more economical in such cases to construct other furnaces, which offer a greater resistance and consume less current for the given 110 volts.

### III. Removal of Undesirable Constituents by Evaporation

**Mechanical Losses During Evaporation.** It is frequently necessary to reduce the volume of the solution containing the substance being analyzed, or to eliminate certain volatile constituents, by evaporation. The factors which determine the rate at which evaporation takes place are the vapor pressure of the solution at

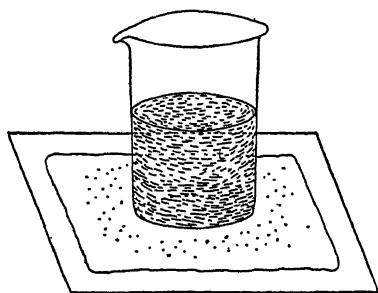


Fig. 15.

different temperatures, the rate at which the vapor formed is carried away from the surface of the liquid, the extent of this surface, and the rate at which heat is supplied to the mixture. The evaporation of solutions at their boiling point necessarily involves the formation of bubbles of the liquid being evaporated at the bottom of the containing

vessel, which rapidly rise and are projected above the surface of the liquid with considerable violence. These bubbles carry with them small quantities of the solution mechanically entrained. This statement is easily proved by the simple experiment represented in Fig. 15. A beaker containing dilute acid is placed on a sheet of blue litmus paper and the acid slowly neutralized with a solution of sodium carbonate. After a few minutes the paper will show a ring of small red spots immediately surrounding the beaker, clearly due to the action of the acid solution projected above the surface of the liquid by the escaping carbon dioxide. This suggests one of the fundamental principles

of quantitative procedure, namely that solutions which are being evaporated in an open vessel should be evaporated somewhat below the boiling point.

If a mixture of a solid and a liquid is being evaporated the phenomenon of "bumping" may occur. This is due to the fact that the solid, especially when it has a high specific gravity, packs together on the bottom of the containing vessel, and bubbles of vapor accumulate between this layer and the bottom of the vessel. Their pressure finally overcomes that of the layer and, in escaping, they throw masses of the mixture out of the vessel with considerable violence. This difficulty does not arise if the temperature is kept somewhat below the boiling point, or if the mixture is stirred vigorously.

Evaporation can be greatly hastened by sucking the vapor formed from the containing vessel by means of a suction pump, or by directing a current of air against the surface of the liquid by means of a force pump. Either device cools the surface appreciably, but as a more efficient heating device can then be used, the rate of evaporation can be greatly increased.

**Methods of Effecting Evaporation.** Two extremes are represented in the methods used to effect rapid evaporations. Either the liquid is placed in a shallow evaporating dish and heated to a temperature somewhat below its boiling point, or it is placed in a flask or narrow beaker and boiled violently. The latter method is somewhat more rapid but requires care and watchfulness on the part of the analyst, and is always subject to the possibility of small mechanical losses. Where the former method is used, a heating device which permits of a rapid and constant control of the temperature is necessary. Direct heating over a flame, even though the vessel is protected from it by a piece of wire gauze, is not to be recommended. The use of a water or steam bath, which insures a temperature somewhat below  $100^{\circ}\text{C.}$ , is usually very satisfactory. A sand bath, or a hot plate, gives higher temperatures and more rapid evaporation, but involves the possibility of mechanical losses.

**Evaporation of Mixtures of Two Volatile Substances.** When two substances which possess appreciable vapor pressures and form homogeneous solutions are mixed together, a reduction in

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the vapor pressures of both constituents takes place, and the sum of the vapor pressures of the two constituents in the mixed vapor phase is less than the sum of the vapor pressures of the pure substances at the same temperature. The extent to which one constituent of such a mixture lowers the vapor pressure of the other varies with different pairs of liquids, but all known examples belong to one of three types. These types can be differentiated most readily by plotting the curves representing the total vapor pressures of the two constituents in the mixed phase corresponding

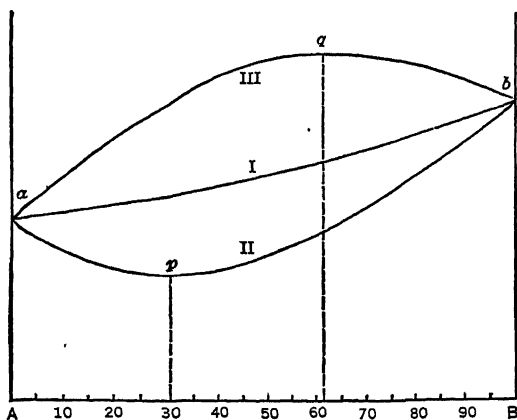


Fig. 16.—Curves representing vapor pressures of mixed liquids.

to all possible mixtures of these constituents. Such curves are represented in Fig. 16, in which the ordinates represent vapor pressures, and the abscissas the comparative amounts of the two constituents *A* and *B*. In Type I the total vapor pressure of the mixture increases continuously from *a*, corresponding to the pure constituent *A*, to *b*, corresponding to the pure constituent *B*. In Type II the total vapor pressure attains a minimum value at *p*, that is, it is reduced by adding *B* to pure *A* or *A* to pure *B* up to the concentration which yields the minimum value *p*. In Type III the total pressure attains a maximum value at *q*, that is, it is increased by adding *B* to pure *A* or *A* to pure *B* up to the concentration which gives the maximum value *q*. Since the boiling points of such mixtures depend directly upon the sum of vapor

pressures of the two constituents the boiling points of mixtures representing Type I decrease continuously as the percentage of that constituent which has the greater vapor pressure increases; whereas the boiling points of mixtures representing Type II attain a maximum and those of Type III attain a minimum at certain concentrations of the two constituents. If then, mixtures belonging to Type II are continuously evaporated, the composition of the mixture changes up to the point at which it has the maximum boiling point; those representing Type III must change up to the point at which it has the minimum boiling point. / Mixtures which are characterized by constant boiling points yield mixed vapor phases in which the relative amounts of the two constituents are the same as in the corresponding liquid phases.

**Removal of Acids by Evaporation.** The mixtures of this kind which are most frequently dealt with in quantitative work are aqueous solutions of acetic, hydrochloric, nitric, and sulfuric acids. The first three of these mixtures belong to Type II. The rate at which any one of these acids is driven out of an aqueous solution by evaporation depends mainly upon the concentration of that acid in the mixed vapor phase. Useful data can therefore be secured by evaporating aqueous solutions of these acids at their boiling points, condensing and collecting the vapor given off at definite time intervals, and determining the composition of the condensed liquid and the solutions from which they were distilled. The results of a series of determinations<sup>1</sup> of this kind are given in the curves of Fig. 17. The ordinates represent the percentages of the various acids in the distillates and the abscissas those of the acids in the corresponding solutions.

These curves at once show the comparative volatilities of the different acids and the concentrations which must be attained before they can be driven out with even reasonable rapidity by evaporation. It will be noted that in evaporating solutions of acetic acid the concentration of the liquid increases at a uniform rate until the residual solution contains about 80 per cent. Solutions of hydrochloric acid concentrate very rapidly at first, then more slowly until a mixture which has a constant maximum boil-

<sup>1</sup> From experimental data obtained by the author.



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ing point of  $110^{\circ}\text{C.}$ , and contains 20.2 per cent of acid is obtained. The behavior of nitric acid resembles that of hydrochloric, but the constant-boiling mixture contains 68 per cent of acid, and boils at  $120^{\circ}\text{C.}$  Sulfuric acid on the other hand is not appreciably volatilized until the solution has attained a concentration of about 98 per cent, which requires a temperature of more than  $250^{\circ}\text{C.}$

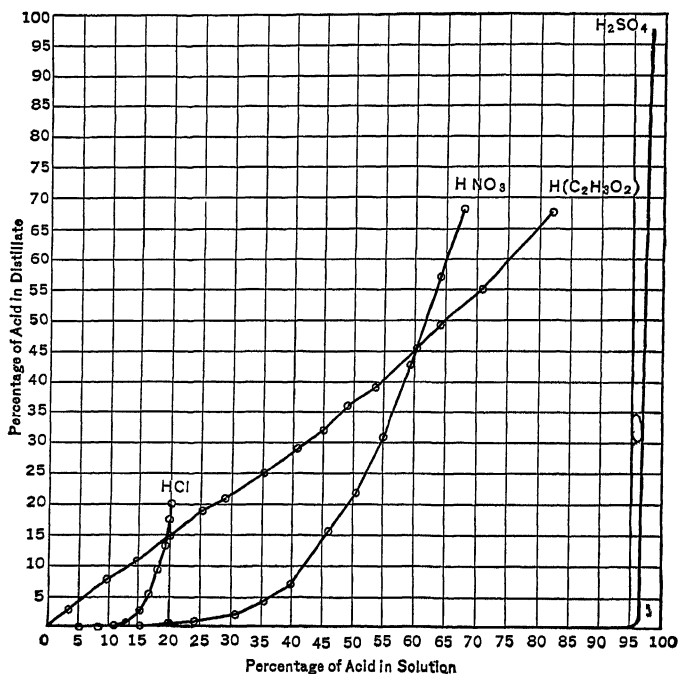
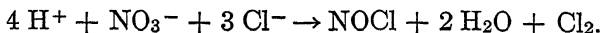


Fig. 17.—Curves showing the changes in concentration which result when dilute acids are distilled.

Complete removal of any of these acids cannot be effected unless the solution is evaporated to dryness; the total amount left in any solution which has been concentrated to a constant boiling point mixture can be calculated from the volume left and the composition of this mixture.

The theory of the removal of acids from solutions containing two or more acids is not so easily followed, for, although the

addition of a second acid reduces the volatility of the first, interaction between the two acids may take place. Thus when the solution contains both hydrochloric and nitric acids, a reaction represented by the equation given below becomes possible:



The reaction constant has a relatively small value, and, unless the concentrations of the two acids are large, but little chlorine is liberated. At high concentrations, and specially at moderately high temperatures, the NOCl formed breaks down into nitric oxide and chlorine, and complete decomposition and expulsion of the acid which is not present in excess is rapidly effected. Hence it is possible to expel either acid by adding an excess of the other acid, and evaporating the solution sufficiently.

### Questions and Problems. Series 2

1. A sample of argol is found to contain 15.42 per cent of hygroscopic water. After drying and mixing it contains 31.25 per cent of potassium bitartrate. What is the percentage of bitartrate in the original sample? *Ans.* 26.43.

2. A lump of ore weighs 500 grams and consists of 20 per cent quartz (sp. gr. 2.8) and 80 per cent pyrite (sp. gr. 5). If the sample is crushed, mixed three times and quartered twice, what is the maximum permissible size of particle for the three crushings in order that the portions removed at the two successive quarterings, and the 0.5-gram portion used for the analysis, shall represent the correct composition of the sample with an error not exceeding 0.1 per cent? *Ans.* 4.7, 2.96, 0.75 mm.

3. How many calories per second would be developed in a furnace whose resistance is (a) 30 ohms, and (b) 60 ohms, when attached to a 110-volt circuit, assuming 1 ampere furnishes one coulomb per second, that one volt-coulomb equals one joule and that one joule equals 4.183 calories? *Ans.* (a) 96.38.

4. What weight of hydrochloric acid should remain in the residual solution obtained by evaporating (a) 120 cc. 3 N hydrochloric acid to 25 cc., (b) 100 cc. 3 N nitric acid to 25 cc.?

5. What should be the composition of the residual solution obtained when a mixture composed of 100 cc. of water, 3 grams of sodium chloride and 7 cc. of concentrated sulfuric acid is evaporated to 10 cc.?

6. If you desired to displace nitrate ion by chloride ion in a solution containing 5 grams of potassium nitrate in 100 cc. of water, what procedure would you use?

## CHAPTER IV

### ✓ CALCULATIONS OF QUANTITATIVE ANALYSIS

#### 1. Calculation of the Results of Gravimetric Processes

**Meaning and Use of Chemical Factors.** The general formula for the calculation of the results of any direct gravimetric process is:

$$\frac{\text{Weight of substance separated} \times f \times 100}{\text{Weight of sample used}} = \text{desired percentage.}$$

In this formula  $f$  represents the factor by which the weight of the separated substance must be multiplied to give the weight of the substance whose percentage is to be reported which is equivalent to the weight of substance which has been separated. Since the substance weighed and the substance reported may have the same chemical formula,  $f$  may have the value 1; usually it has a different value, which may be either greater or less than 1, and can be calculated from the atomic and molecular weights of the substances concerned. If a precipitate of  $\text{Mg}_2\text{P}_2\text{O}_7$  has been separated, and it is desired to report the percentage of phosphorus present, it would be reasoned that every molecule of  $\text{Mg}_2\text{P}_2\text{O}_7$  separated represents two atoms of phosphorus in the sample, and hence the desired factor is obtained by dividing two times the atomic weight of phosphorus by the molecular weight of magnesium pyrophosphate. If a precipitate of  $\text{Fe}_2\text{O}_3$  has been separated and it is desired to report the  $\text{Fe}_3\text{O}_4$  present, the reasoning would be that for every three molecules of  $\text{Fe}_2\text{O}_3$  found, two of  $\text{Fe}_3\text{O}_4$  must have been present, and the proper factor to employ is  $2 \text{ Fe}_3\text{O}_4 \div 3 \text{ Fe}_2\text{O}_3$ . It should be especially noted that the number and character of the reactions concerned in the production of the substance which is separated from the sample are of no significance. When a substance which contains  $\text{Fe}_3\text{O}_4$  is analyzed

by separating  $\text{Fe}_2\text{O}_3$  from it, it can be assumed that, since the process is a quantitative one, all of the iron present as  $\text{Fe}_3\text{O}_4$  is transformed into  $\text{Fe}_2\text{O}_3$ , and that no additional iron in any form is introduced.

In certain procedures the separated substance weighed is not actually present in the original sample. Thus in the determination of potassium in a sample containing potassium sulfate the potassium may be separated as potassium chloroplatinate,  $\text{K}_2\text{PtCl}_6$ , the latter converted into solid potassium chloride, platinum, and gaseous chlorine by heating, the potassium chloride washed out, and the residual platinum weighed. The factor which should be used in this determination is clearly the number found by dividing the molecular weight of potassium sulfate by the atomic weight of platinum. In this and all other determinations the factor represents the ratio between equivalent amounts of the substance reported and the separated substance weighed.

**Experimental Determination of Chemical Factors.** The value of  $f$  can also be determined experimentally by submitting a sample containing a known percentage of the substance which is to be reported to the given analytical process and calculating the ratio of the weight of the substance known to be present in the sample to the weight of product separated. An empirically determined factor of this kind is subject to errors of the same kind and magnitude as those concerned in the actual determination. If the process is a complex one, in which subsidiary reactions are possible, and large errors of any kind are to be expected, the empirically determined factor is the logical one to use, because the errors involved in the actual determination are partly or wholly counterbalanced. If the process is based upon a few simple and definite reactions and is not subject to any large errors, the calculated factor should be used, since it is based upon experimental work of much greater accuracy, namely the atomic weights made use of, than that attained in the determination of the empirical factor.

**Form in which Results are Reported.** The form in which the results of an analysis are reported admits of some degree of choice and this depends largely upon the purpose for which the analysis is made. In general, it is advisable to report all results in such a form as will indicate most nearly the actual composition of the

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sample. Thus, if nitrogen is determined and reported as such, there is no means of knowing which one of the various forms in which that element may be combined is represented, whereas if the report is in terms of  $\text{NH}_3$ ,  $\text{N}_2\text{O}_5$ , or  $\text{N}_2\text{O}_3$ , the presence of corresponding percentages of ammonia, of nitrates, or of nitrites is clearly shown. Since oxygen, unless it is in the free condition, is but rarely determined, it is customary to report it in combination with the metals or metalloids actually present. This makes it readily possible to show the degree of oxidation of these elements and to account for everything present, that is to make the analysis sum up to 100 per cent. Thus, in the analysis of crystallized ferrous sulfate, it is desirable to report the percentages of  $\text{FeO}$ ,  $\text{SO}_3$  and  $\text{H}_2\text{O}$  rather than  $\text{Fe}$ ,  $\text{S}$  and  $\text{H}$ .

It should be noted that if salts, such as chlorides or sulfides, which do not contain oxygen, are present, and all of the bases present are reported as oxides, more oxygen will be included in the summation than is actually present. The proper correction is then made by subtracting the oxygen equivalent of the chlorine and sulfur from the summation; this then appears in the summary as "less oxygen due to chlorine and sulfur."

When a solution is submitted to analysis, it is customary to report the ions present. Formerly an attempt was made to calculate and report the probable salts present, that is to combine the acidic and basic radicals according to certain arbitrary rules. This method is misleading if the validity of the electrolytic dissociation theory is granted.

**Precision in the Calculations Used.** Although the mathematical operations of most quantitative processes are simple, an undue expenditure of effort in attaining an unnecessary degree of accuracy in making these calculations should be avoided. There are certain conventional rules which can be used without danger of introducing important errors in the final results of such calculations.

First, in recording the number representing the results of experimental work, do not use more digits than the accuracy of the experimental work justifies. Usually the last digit to the right of the decimal point represents a doubtful value, and there is no reason for including more than one doubtful digit. The swings

of the pointer of the balance may involve an error of one or two units in the first decimal place and no digits in the second or third decimal place should ever be written down. Similarly, in reading the results of a weighing made with the usual type of analytical balance, there is no justification for recording any digits beyond the fourth decimal place; to do so would give an erroneous idea of the accuracy of the result.

Second, in carrying out the various mathematical operations required, discard all but four significant figures at each stage of the process. By significant figures are meant the number of digits to the right and including the first integer in the number as written, provided the number includes only one doubtful integer, that is, agrees with the first rule. If the number is 4.710 there are four significant figures, if it is 0.04710 there are still only four significant figures since the first zero merely fixes the position of the decimal point. Even if the greatest attainable accuracy were demanded, there would be no justification for retaining more than one doubtful integer in any of the operations to which the quantities used are submitted. Furthermore, there are but few quantitative processes in which the final result is accurate to more than one part per thousand and hence there is but little justification for using a method of calculation in which more than four significant figures are retained.

Third, if a series of results representing the same measurement have been obtained, do not reject any one of them in calculating the mean value unless the total number is as great as five. There is no justification for rejecting any result because it differs greatly from the others unless it is known that certain unusual errors entered into that result or unless the total number of observations is large enough to justify the belief that it was an erratic result.

**Simplification of Calculations.** In making quantitative calculations in accordance with the preceding rules greater speed and less probability of error will be attained by the use of four or five place tables of logarithms. The usual common 10-inch slide rule should be used only in making rough estimates and in checking results for large errors.

If many determinations are made by the same process, and therefore the same factor is used, time can be saved by preparing a

table showing the values of a series of multiples of the factor used and interpolating between them for the multiples actually needed. Still another method of arriving at the same result is to plot a graph, in this case a straight line, showing the relation between the factor and multiples of it. Many handbooks containing tables of this kind and other information frequently needed by the analyst are available.<sup>1</sup>

Another device, largely used in commercial laboratories, is to employ "factor weights." If the quantity of sample employed is made equal to  $f$  of the general formula (see page 42), the desired percentage is exactly 100 times the weight of the separated substance. If the factor weight is larger or smaller than it is desirable to use, a simple fraction or multiple of it can be used with nearly equal advantage.

✓ **Calculation of Indirect Determinations.** It is sometimes advantageous to analyze certain kinds of mixtures by so-called "indirect methods." Thus, it is possible to calculate the percentages of sodium and potassium chloride in mixtures of these salts from the total percentage of chloride in the mixture, which can be easily determined with great accuracy. If the percentage of sodium chloride in such a mixture be represented by  $x$ , then  $100 - x$  must represent the percentage of potassium chloride, and if the percentage of chlorine in it be represented by  $a$ , the following relation is true:

$$x \frac{\text{Cl}}{\text{NaCl}} + (100 - x) \frac{\text{Cl}}{\text{KCl}} = a.$$

From this the percentages of sodium and potassium chlorides are easily calculated.

Another method of attaining the same result consists in ascertaining the factor representing the relation between a known weight of the mixture and the weight obtained when the chlorides present are completely changed into sulfates, which change is easily effected by evaporating with an excess of sulfuric acid. If

<sup>1</sup> Handbook of Chemistry and Physics. The Chemical Rubber Co.

this factor is represented by  $b$ , the following relation is true:

$$x \frac{\text{Na}_2\text{SO}_4}{2 \text{NaCl}} + (100 - x) \frac{\text{K}_2\text{SO}_4}{2 \text{KCl}} = 100 b.$$

The desired percentages can thus be easily calculated.

The former process is based upon the difference between the ratio of Cl to NaCl and the ratio of Cl to KCl. This amounts to only 0.131, and an error in the determination of chlorine in the unknown mixture is multiplied by  $1 \div 0.131$  or 7.64. This suggests the chief objection to such processes, that is, that relatively small errors in the determination of chlorine in the mixture and the presence of small amounts of additional substances make large errors in the final results. The second process depends upon the difference between the ratio of  $\text{K}_2\text{SO}_4$  to 2 KCl and of  $\text{Na}_2\text{SO}_4$  to 2 NaCl, which has the value 0.0465, and consequently is less desirable than the first process.

## II. Methods of Estimating the Accuracy of Results

**Meaning and Use of Percentage Error.** All quantitative processes involve certain unavoidable errors and it is desirable to be able to estimate the probable accuracy of the determinations made by any quantitative process. It is obvious that the ratio between the actual error and the magnitude of the number reported represents the only correct standard by which to judge of the accuracy of a result. An error of 0.1 per cent in the analysis of a sample containing 50 per cent represents a higher degree of accuracy than an error of 0.1 per cent in the analysis of a sample containing 10 per cent. In order to correctly estimate the comparative accuracy of these two results they must be expressed as ratios between the error and some standard percentage. If the standard percentage chosen is 100 the resulting numbers are percentage errors. If this standard is applied to the first result we obtain  $(0.1 \div 50)100 = 0.20$ , and if applied to the second we obtain  $(0.1 \div 10)100 = 1.0$ . Hence the percentage error of the second result is five times that of the first.



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Another method of expressing the relative accuracy of numerical results is to give the quantity representing the error the value one, and to calculate the number which bears the same relation to one as the correct percentage bears to the error reported. Applied to the two results quoted it can be said that the first result involves an error of one part in 500 and the second of one part in 100.

**Sources of Error in Quantitative Determinations.** The total error of a determination depends upon the separate errors in each of the different operations used in the process and the manner in which these separate errors are combined in the final result. For the general case of a simple process, which involves separation of a product, the important errors are those which arise (a) in determining the weights of the sample and separated product, (b) in separating completely a product of absolute purity (c) in calculating the chemical factor used. Since error (a) usually involves a difference between a charged and an empty container, and error (b) assumes multiplication and division, the effect of these mathematical operations must also be considered.

The net error of the entire process can be ascertained by applying it to some substance which contains a known percentage of the substance being determined, that is, a substance whose purity is so great and whose composition is so well established that it becomes a "primary standard." Absolute purity is an ideal which is never actually realized and to this extent this procedure fails to give a perfect estimate of the accuracy of a quantitative procedure. Usually the discrepancy is too small to be of significance, but there are methods in use for which even the best obtainable primary standard is decidedly impure.

It should be noted also that the difference between any one result and the theoretically calculated result gives no adequate idea of the probable accuracy of a process since chance enters into certain of the errors and a fortuitous combination of these errors may indicate zero error even though the process be far from perfect. At least five results should be available before a proper evaluation of the process can be made. The numerical expression for the accuracy is then found by calculating the mean or average of all the results obtained, subtracting this mean suc-

cessively from each separate determination, and calculating the average of the differences without regard to their signs. This result is known as the mean deviation of the method. The difference between the mean-value and the theoretical result taken into conjunction with the mean deviation of the method furnish the best data usually available from which to estimate how large an error is to be expected in the use of a given quantitative method.

**Determinate and Indeterminate Errors.** A comprehensive understanding of the accuracy of a quantitative procedure necessitates a detailed study of the errors in each of the operations and the combination of these errors in a final result, which represents the accuracy of the entire procedure, according to the proper mathematical principles. Certain errors, such as those resulting from inequality in the length of the arm of the balance used, failure to correct weights for buoyancy, or errors in the atomic weights, always have the same sign and the same percentage value. The percentage error of the final result will always include the net sum of all the percentage errors belonging to this category. These are called determinate errors and, in most cases at least, are too small to be of much significance in those quantitative determinations whose details of procedure have been carefully established.

Certain other errors depend upon the judgment and skill of the analyst. These include such items as incorrect readings of the swings of the pointer of the balance, mechanical losses or additions to the separated substance, and failure to ignite the separated substance for the proper length of time or to the proper temperature. These errors may be positive in one determination and negative in another and of variable magnitude. All the operations used in a quantitative process involve the possibilities of such errors.

**Calculation of the Mean Probable Error.** Certain of the items which determine the total error of the final result of a quantitative process affect all processes equally. Thus the indeterminate feature of the errors in weighing the sample is the same for all processes provided the same weight of sample is used. It may be determined for any given observer using the same balance and method of procedure by making a large number of independent determinations of the same mass of sample. The result of such a

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series of determinations is best expressed as the "mean probable error," the calculation of which will be most easily comprehended by use of a graphical method of procedure. The deviation of all the result from the mean are first classified as to sign and magnitude, and the results which fall within each of the limits adopted in the chosen scheme of classification are counted. The proper positions of the points on a horizontal line defining the limits of these classes are next found, and perpendiculars erected at the proper points on the horizontal line whose lengths are proportional to the total number of determinations which fall within each of these limits. The curve which is obtained when the ends of these perpendiculars are joined gives a distribution diagram or "frequency curve." Such curves, of which Fig. 18 is an illustration,

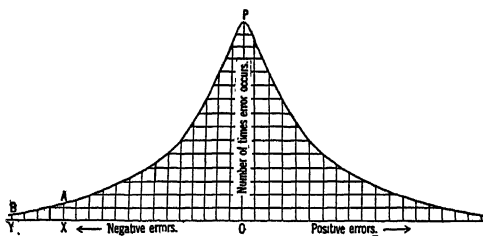


Fig. 18.—An ideal frequency curve illustrating indeterminate errors.

assume a characteristic bell-like shape and are symmetrical with respect to the ordinate passing through the point representing zero deviation provided all of the errors concerned are indeterminate rather than determinate. This curve shows the characteristic features of all measurements whose variations are the result of chance only. It is obvious, then, that for a sufficiently large number of measurements the number of times a plus error is made equals the number of times a minus error is made, and the number of large errors is small while very small errors occur frequently. The actual form which such curves assume, which can be expressed by a simple mathematical formula, varies with the degree of accuracy represented. If the degree of precision attained is high the hump of the curve is high and narrow rather than low and broad. In proportion as the number of measurements representing small deviations is large will the area of the space below

the bell-shaped portion of the curve be large as compared with that below the entire curve. The number representing the probability that the error of any single determination will exceed a certain limit can be calculated. If, for example, we desire to calculate the probability that the error of any single determination will not exceed the value  $x$ , we simply determine the ratio between the area  $OxAP$  and  $OyBP$ . This ratio is a measure of the ratio between the total number of determinations in which the deviation did not exceed  $x$  and the total number of determinations.

Further, if we assume that a sufficiently large value for the probability that the error will not exceed a certain value is for most purposes equivalent to certainty, we can calculate the "probable error" of a single determination. If, for example, the ratio  $OxAP : OyBP = 80 : 83$ , the number of determinations in which the deviation exceeds  $x$  is so small that it is fairly safe to assume that the probable error of any single determination does not exceed  $x$ . By convention a probability of  $99 : 100$  is commonly assumed to represent certainty, and the calculation of the probable error of a process involves finding the largest value of  $x$  for which the total number of errors which do not exceed  $x$  divided by the total number of determinations equals  $99 \div 100$ .

The mean probable error of all the indeterminate errors having been found these are then combined to give the mean probable error of the final result in accordance with two fundamental principles. First, the probable error of a result which involves the addition or subtraction is found by extracting the square root of the sum of the squares of the probable errors of the quantities added or subtracted. Second, the probable error of a result which involves the multiplication or division of two quantities is found by taking the square root of the sum of the squares of the percentage errors of the quantities multiplied or divided. Let us suppose for example that the results of a series of measurements in a given analytical procedure are  $A, B, C, D$ , and the respective probable errors are  $a, b, c$ , and  $d$ . If the calculation in which these results are combined involves addition and subtraction only then the mean probable error of the entire procedure is found by means of the expression:

$$\text{Mean Probable Error} = \sqrt{a^2 + b^2 + c^2 + d^2}.$$

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If on the other hand the calculation involves only multiplication and division the corresponding expression becomes:

Mean Probable Percentage Error

$$= \sqrt{\left(\frac{100a}{A}\right)^2 + \left(\frac{100b}{B}\right)^2 + \left(\frac{100c}{C}\right)^2 + \left(\frac{100d}{D}\right)^2}.$$

Both of these formulas are derived from the theory of probability; the second one is a simplified form of a more elaborate expression, but is sufficiently accurate for most uses. In using these formulas for processes which involve both addition or subtraction and multiplication or division they must be applied to the two groups of operations successively.

**Practical Illustration.** The application of these principles to a typical quantitative process will be shown by consideration of a specific case. It will be assumed that  $\text{MgO}$  in a sample is determined by separating and weighing all of the magnesium present as  $\text{Mg}_2\text{P}_2\text{O}_7$  and that the actual analysis involved the following measurements:

Weight of empty watch glass. . . . .	8.5341 gm. $\pm$ 0.0002
“ “ watch glass plus sample. . . . .	9.3863 gm. $\pm$ 0.0002
“ “ empty crucible. . . . .	6.5148 gm. $\pm$ 0.0002
“ “ crucible plus precipitate. . . . .	7.6720 gm. $\pm$ 0.0002

It will be further assumed that the atomic weight of magnesium is  $24.32 \pm 0.04$ , of phosphorus is  $31.03 \pm 0.03$  and of oxygen is  $16 \pm 0.0$ . The calculated percentage of  $\text{MgO}$  is:

$$\frac{(7.6720 - 6.5143) \cdot (2 \times 24.32 + 2 \times 16) 100}{(9.3863 - 8.5431) \cdot (2 \times 24.32 + 7 \times 16 + 2 \times 31.03)} \quad \text{or} \quad 49.72.$$

The probable error in the weight of sample used, namely  $0.8432$ , becomes  $\sqrt{(0.0002)^2 + (0.0002)^2}$  or  $0.00028$  and the probable percentage error becomes  $0.0385$ . Similarly the probable error in the weight of the precipitate obtained, namely  $1.1572$  is also  $0.00028$ , but the percentage error becomes  $0.024$ .

The probable error in the numerator of the chemical factor used, namely  $2\text{Mg} \frac{1}{2} \text{Mg}_2\text{P}_2\text{O}_7$  becomes  $\sqrt{2(0.04)^2 + 2(0.00)^2}$  or  $0.056$  and the corresponding percentage error  $0.07$ . Similarly the probable error in the denominator of this factor becomes

$\sqrt{2(0.04)^2 + 2(0.03)^2 + 7(0.00)^2}$  or 0.071, and the corresponding percentage error 0.032.

The mean probable percentage error of the final result must be  $\sqrt{(0.0335)^2 + (0.0244)^2 + (0.07)^2 + (0.032)^2}$  or 0.087. This would give a probable departure from the calculated percentage of 0.043.

It should be noted that there are certain other errors, such as those due to solubility of the precipitate and contamination of the precipitate with impurities, which are not considered in this calculation.

### ✓ III. Calculation of Molal Concentrations

**Molal Concentrations in Simple Solutions.** The completeness of the reactions upon which quantitative processes are based depends upon the molal concentrations of the substances concerned in such reactions, and therefore it becomes necessary to be able to calculate such quantities. The term mole signifies a particular amount of some substance whose chemical formula is known; namely, that number of units of weight which is equal to the number of units in the atomic or molecular weight of that substance. A solution of molal concentration contains one mole of the dissolved substance in a unit volume of the solution. Usually the gram is the unit of weight and the liter the unit of volume adopted. It will be assumed throughout this book that molal concentration means moles per liter of solution. Hence we have:

Molal Concentration

$$= \frac{\text{Wt. of substance in grams}}{\text{Mol. or At. Wt. of substance}} \times \frac{1000}{\text{Vol. of mixture in cc.}}$$

Molal concentrations will be indicated by enclosing the symbol of the substance concerned in parentheses.

In order to calculate the molal concentrations of the ions in solution, it is necessary to know what fraction of the electrolyte is in the dissociated condition. If it can be assumed that the dissociation is complete, the concentration of each of the different ions present must equal the total molal concentration of the

electrolyte or some simple multiple of it. Thus, since the dissociation of salts in solutions of moderate concentration is practically complete, the concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  in solutions of sodium chloride of moderate concentration is the same as that of the total number of moles of sodium chloride present. The concentration of  $\text{Al}^{+++}$  in a molal solution of aluminum chloride is also equal to that of the aluminum present, but the concentration of  $\text{Cl}^-$  is three times that of the aluminum chloride because each molecule of it yields three chloride ions. It will be shown in Chapter V how the degree of dissociation of partially ionized electrolytes can be calculated from their dissociation constants. These factors must enter into the calculation of the ionic concentrations resulting from the dissociation of partially dissociated electrolytes.

**Molal Concentrations in Complex Solutions.** If the solution contains a number of electrolytes, the calculation of the concentrations of all the molecular species present is more difficult since, as will be shown in Chapter V, one electrolyte may diminish the degree of dissociation of another. Calculation of the concentration of the ions present in mixtures composed of electrolytes which form insoluble compounds is easily made and is of constant use in studying the theory of quantitative processes. We will assume that it is desired to know the concentrations of all the molecular species in a mixture composed of 0.642 gram of ferric chloride and 0.4 gram of potassium hydroxide in a total volume of 700 cc., and that the solubility of the ferric hydroxide formed is negligible. We first find the number of moles of ferric chloride to be  $0.642 \div 162.2$ , or 0.00396 and of potassium hydroxide to be  $0.4 \div 56.1$ , or 0.00713. Since each mole of ferric ion requires three moles of hydroxyl ion to precipitate it, there must be  $0.00396 - (0.00713 \div 3)$  or 0.00158 mole of ferric ion still in the solution in addition to all the chloride ion and all the potassium ion. Hence the solution contains

$$0.00158 \times \frac{1000}{700} = .00226 \text{ mole of } \text{Fe}^{+++}$$

$$0.00396 \times 3 \times \frac{1000}{700} = .0169 \text{ mole of } \text{Cl}^-$$

$$0.00713 \times \frac{1000}{700} = .0102 \text{ mole of } \text{K}^+$$

In such calculations only approximate values are needed and extreme accuracy is unnecessary. A test of the accuracy of the final result is that the sum of the concentrations of the plus and minus charges must be zero.

#### IV. Questions and Problems. Series 3

1. Calculate the percentage error of a determination of manganese in an alloy in which the correct percentage is 2.43 and that found is 2.31. What is the error expressed in proportional parts?

Ans. 4.93 per cent and one part per 20.3.

2. How many significant figures are there in the following numbers: 714.20, 0.0413, 7000, 4.0001?

Ans. 5, 3, 4, 5.

3. The different results obtained by an analyst in determining silicon dioxide in a rock were 67.62, 67.51, 67.36, 67.25. (a) What results, if any, should be rejected in calculating the mean value? (b) Calculate the mean deviation. (c) Assuming that a determination of  $\text{SiO}_2$  in a "primary standard" composed of pure quartz and the same bases as the rock gave 66.12 instead of the true value of 66.24, what is the probable correct result?

Ans. (a) none, (b) 0.13, (c) 67.44.

4. What is the mean probable error of the sum of three weights, namely  $0.4123 \pm .0001$ ,  $6.412 \pm .002$ ,  $2.100 \pm .003$ ?

Ans. .0036.

5. What is the mean probable error of the factor used to calculate the antimony in a weight of  $\text{Sb}_2\text{S}_3$ , assuming the atomic weight of antimony is  $121.77 \pm 0.1$  and of sulfur is  $32.065 \pm .005$ ?

Ans. 0.0005.

6. Calculate the chemical factors which should be used in converting (a)  $\text{K}_2\text{PtCl}_6$  into  $\text{K}_2\text{O}$ , (b)  $\text{Mg}_2\text{P}_2\text{O}_7$  into  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , (c)  $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  into  $\text{Al}_2\text{O}_3$ .

Ans. (a) 0.1937, (b) 1.826, (c) 0.1124.

7. A certain mixture is known to contain pure  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgI}_2$  only. The weight of  $\text{Mg}_2\text{P}_2\text{O}_7$  obtained from 1.324 grams is 1.2174 grams. What are the percentages of the two components of the mixture?

Ans. 37.36 per cent  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 62.64 per cent  $\text{MgI}_2$ .

8. Calculate  $(\text{Pb}^{++})$  and  $(\text{Cl}^-)$  in a solution made by dissolving 0.3 gram of  $\text{PbCl}_2$  in 750 cc. of water, assuming the fraction dissociated is 0.68.

Ans.  $(\text{Pb}^{++}) = 0.00097$ ,  $(\text{Cl}^-) = 0.00194$ .

9. A solution containing 5.6 grams of  $\text{NH}_4\text{OH}$  is added to one containing 6.4912 grams of  $\text{FeCl}_3$  and 0.98 gram of  $\text{H}_2\text{SO}_4$ . If the final volume is 300 cc., what are the concentrations of all the substances present in the solution, assuming the dissociation of  $\text{NH}_4\text{OH}$  is negligible.

Ans.  $(\text{SO}_4^{--}) = 0.0333$ ,  $(\text{NH}_4^+) = 0.4666$ ,  $(\text{NH}_4\text{OH}) = .0666$ ,  $(\text{Cl}^-) = 0.4$ .



## CHAPTER V

### THE FACTORS WHICH DETERMINE CHEMICAL EQUILIBRIUM

#### I. General Features

**Equilibrium and Reaction Velocity.** When two substances react chemically they are in a condition of unstable equilibrium with respect to each other; when there is no further change in the relative masses of these substances, "equilibrium" has been reached. This condition is also defined by the statement that the "reaction velocity" is zero, where the term reaction velocity is defined as the net mass of one or both of the original substances transformed into new substances during some unit of time. The velocity of many chemical reactions, especially those designated as "explosive," must be expressed by very large numbers, even when the unit of time adopted is the second; that of other reactions is so small that the day is the more convenient unit to employ. Most of the reactions which are of importance in quantitative analysis have velocities which are too great to be determined with even approximate accuracy.

**Homogeneous and Heterogeneous Equilibrium.** In discussing the subject of chemical equilibrium and reaction velocity, a very important factor to be considered is whether all the reacting substances, and all of the products of the reaction exist in the same phase and the nature of this phase. (For a definition of the term phase see page 3.) If all the substances concerned are gases, or if all remain dissolved in the same liquid phase throughout the reaction period, their respective concentrations remain uniformly distributed throughout the entire mass, and the resulting equilibrium is called "homogeneous." If the reacting substances exist as two distinct phases, or if two distinct phases result as the reaction progresses, the resulting equilibrium is called "heterogeneous."

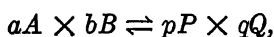
In homogeneous equilibrium, the reaction velocity is uniform at all points throughout the reacting mass; in heterogeneous equilibrium, the reaction velocity may differ in the different phases, and may be reduced practically to zero except at the surfaces of contact between the different phases.

A condition of perfect equilibrium between the different phases of a heterogeneous system must result if they are allowed to remain in contact for a sufficient length of time, but the extent of the surfaces of contact between these phases and the rates at which the products of the reaction diffuse away from the immediate neighborhood of these surfaces greatly influences the time needed for the establishment of this equilibrium.

**Factors Affecting Chemical Equilibrium.** There are four factors which materially affect the direction and the rate of progress of chemical reactions: first, the chemical properties of the reacting substances; second, the concentrations of the substances taking part in the reaction; third, the temperature; and fourth, the pressure.

As regards the first of these factors our present knowledge suggests the theory that among the other specific properties with which every substance is endowed is a certain intensity of chemical energy or chemical potential, and, in general, any two substances tend to react with each other to an extent directly dependent upon the difference between the intensity of the chemical energy associated with them. In other words, there is a universal tendency for the equalization of chemical intensities just as there is a universal tendency for the equalization of heat intensities, and no reaction takes place which does not involve a reduction in the chemical potential of the mixture.

The action of the second factor is expressed in the "Law of Mass Action," which states that the speed of the reaction between any two substances in a mixture is proportional to the product of the concentrations of these substances in that mixture, where the concentrations are expressed in moles per unit of volume. For a reaction between the substances *A* and *B* which unite to form the substances *P* and *Q* such as



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the law of mass action equates the two reaction velocities at equilibrium as follows:

$$(C_A)^a \cdot (C_B)^b \cdot k = (C_P)^p \cdot (C_Q)^q \cdot k'.$$

In this expression  $(C_A)$   $(C_B)$ , etc., represent the concentrations of these molecules;  $a$ ,  $b$ , etc., the number of molecules of these substances concerned in the reaction;  $k$ , a constant expressing the speed of the reaction between  $A$  and  $B$ ; and  $k'$  a constant expressing the speed of the reaction between  $P$  and  $Q$ . Since  $k$  and  $k'$  are both constants, the expression can be simplified by dividing by  $k'$  and substituting  $K$  for  $k \div k'$ . We then have

$$K = \frac{(C_P)^p \cdot (C_Q)^q}{(C_A)^a \cdot (C_B)^b}.$$

We might have simplified by dividing by  $k$ , in which case  $k' \div k$ , or  $K$ , would have a value represented by the reciprocal of that given in the above expression. Throughout this book the former procedure will be employed, that is, where  $K$  is referred to, it will be understood to represent the constant obtained when  $K$  appears on the left of the sign of equality in the mass-law expression.

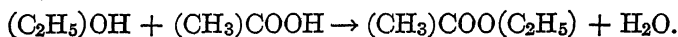
It is evident that  $K$  represents a ratio whose value depends upon the specific properties of the four substances,  $A$ ,  $B$ ,  $P$ , and  $Q$ , and not upon the concentration in which any one or more of them exist in the mixture. If a mixture is made in which  $(C_P)^p \cdot (C_Q)^q \div (C_A)^a \cdot (C_B)^b$  exceeds  $K$ ,  $(C_A)$  and  $(C_B)$  must increase and  $(C_P)$  and  $(C_Q)$  must decrease until the mass-law expression is satisfied, that is, the reaction must progress from right to left. In general, if the value of  $K$  is large, the predominating tendency is for the reaction to proceed from left to right; if it is a small fraction of unity, the predominating tendency is for it to progress from right to left. Since the value of  $K$  determines to a large extent the direction in which reactions progress, it is called the "reaction constant" or "equilibrium constant."

The effect of temperature upon a reaction depends upon whether the reaction absorbs or liberates heat. Increasing the temperature displaces the equilibrium in the direction of that reaction which

absorbs heat, that is, it increases  $K$  if heat is absorbed when the reaction progresses from left to right; it displaces equilibrium in the reverse direction if heat is given out, that is, it decreases  $K$  if heat is liberated when the reaction progresses from left to right.

Increasing the pressure to which the reacting mass is subjected decreases its volume and therefore must increase the concentrations of all the active reagents by the same factor. If the reaction itself does not involve a change in volume increasing the pressure increases the value of  $(C_A)^a \cdot (C_B)^b$  and  $(C_P)^p \cdot (C_Q)^q$  equally and therefore causes no change in equilibrium. If the reaction is associated with a decrease in volume increasing pressure decreases the value of the ratio  $(C_P)^p \cdot (C_Q)^q \div (C_A)^a \cdot (C_B)^b$ , which necessitates an increase in  $(C_P)$  and  $(C_Q)$  at the expense of  $(C_A)$  and  $(C_B)$ ; if associated with an increase in volume the reverse change must take place.

An Illustration of Homogeneous Equilibrium. The manner in which the factors named in the preceding section affect a simple reaction involving homogeneous equilibrium can be most easily comprehended by considering a specific case, such as the action between acetic acid and ethyl alcohol. These substances, as well as the products of their interaction, are soluble in each other to an unlimited extent. When acetic acid is added to alcohol, the resulting reaction is represented by



If water is added to ethyl acetate, alcohol and acetic acid are produced,—that is, the reaction progresses in the reverse direction when the concentrations of water and ethyl acetate are large. If either of the two mixtures is allowed to stand until equilibrium has been attained, the concentrations of the four substances in the mixture must be in accord with the expression:

$$K = \frac{(C_4H_8O_2) \cdot (H_2O)}{(C_2H_4O_2) \cdot (C_2H_6O)},$$

in which, as in all subsequent pages of this book, a chemical formula enclosed in parentheses or brackets designates concentrations of the corresponding substances expressed in moles per liter. The value of  $K$  for this reaction has been determined experi-

mentally by making an analysis of a number of mixtures of the four reagents after equilibrium has been attained. At  $25^{\circ}\text{C}$ . the value of  $K$  is approximately four. Knowing the value of  $K$ , it becomes possible to ascertain by a simple calculation the extent to which reactions between known amounts of acetic acid and alcohol, or between known amounts of ethyl acetate and water, will progress before equilibrium is attained.

Let us start with 240 grams, 4 moles of acetic acid and 138 grams, 3 moles, of alcohol, and assume that  $x$  moles of water, and therefore  $x$  moles of ethyl acetate, are produced before equilibrium is reached. The volume change associated with the reaction is relatively small and may be neglected without serious error. If the volume of the mixture is  $V$ , the concentration of acetic acid at equilibrium is  $\frac{4-x}{V}$ , of alcohol is  $\frac{3-x}{V}$ , of water and ethyl acetate is  $\frac{x}{V}$ . The mass-law expression then becomes

$$\frac{4-x}{V} \cdot \frac{3-x}{V} \cdot 4 = \frac{x}{V} \cdot \frac{x}{V} \quad \text{or} \quad 3x^2 - 28x = -48.$$

When the quadratic equation is solved for  $x$  two possible values, namely 7.066 and 2.266 are found. Since 7.066 is clearly impossible the equilibrium mixture must consist of 2.266 moles of ethyl acetate and of water, 1.736 of acetic acid and 0.736 of alcohol. If the original mixture had contained 54 grams, 3 moles, of water, the mass-law expression would have been

$$\frac{4-x}{V} \cdot \frac{3-x}{V} \cdot 4 = \frac{(3+x)}{V} \cdot \frac{x}{V}$$

from which it can be calculated that  $x = 1.9$  moles.

Since the formation of ethyl acetate and water liberates heat, increasing the temperature decreases the value of  $K$  and the amount of ethyl acetate and water formed from a given amount of acetic acid and alcohol.

Since gaseous substances are neither produced nor used up, at least in significant amounts, the volume change is small, and

therefore pressure has but little effect upon the value of  $K$  and the completeness of the reaction.

**Reversible and Irreversible Reactions.** In the reaction discussed in the preceding section, the constant  $K$  has a moderately large value only. This means that the tendency for the reaction to take place in one direction is greater than the tendency to take place in the reverse direction, but both tendencies are easily measurable. Expressed differently, if the original mixture contains equal concentrations of the four reagents, appreciable amounts of all four substances are left in the equilibrium mixture. In other reactions the value of  $K$  may be large, and such reactions are practically "complete,"—that is, only negligible amounts of the reacting substance are left in the equilibrium mixture if equivalent amounts are present at the outset.

There are many reactions which cannot be made to take place in the reverse direction, because the speed of the reverse reaction is zero. It is readily possible, for example, to cause oxygen to combine with very many complex organic compounds to form water and carbon dioxide, but very few of these compounds can be synthesized from water and carbon dioxide. Such processes are designated as "irreversible." Although the concentrations of the products formed increase as the reaction progresses, there is no measurable tendency for these products to reform the original substances. Such reactions proceed in the given direction until, owing to decreasing concentrations of the reacting substances, the rate of reaction becomes zero or too small to be recognized.

The accuracy of quantitative processes, which depend upon the use of chemical reactions, is largely determined by the extent to which the substance being determined is transformed into the desired products. Therefore, only those reactions which are reversible and have large equilibrium constants, or which are irreversible, can be used in such processes. Variations in the concentrations of the reacting substances and in the temperature may be used to displace the equilibrium of reversible reactions in the desired direction.

**Reaction Velocity and Catalysis.** There is no relation between the rate at which a reaction reaches equilibrium and the magnitude of its equilibrium constant. Many reactions are known whose

equilibrium constants are large, but which attain a condition of equilibrium so slowly that they are of little use in quantitative analysis. Since the speed of all reactions should be more than doubled for every increase of 10 C. degrees in the temperature of the reacting mass, an increase in temperature may also be used to further the completeness of such reactions. The speed of certain reactions is increased in an abnormal manner by certain substances and decreased by others. The former are known as positive and the latter as negative catalysts. Very small concentrations of a catalyst may produce very marked effects, and as they do not suffer any appreciable change in concentration, these catalysts must react indirectly, that is, form one or more intermediate compounds with the reacting substances, which at once decompose into the original catalyst and the desired end product. According to this theory, the speed of the reaction as a whole is increased because the speeds of the intermediate reactions exceed that of the direct reaction between the original substances. Catalysts have no effect upon the value of the equilibrium constant, but increase the speed at which a condition of equilibrium is attained.

Many insoluble substances are effective catalysts, and the effect to which they give rise is related to the amount and the character of the solid surface which is exposed to the reacting system.

**Reactions Involving Heterogeneous Equilibrium.** Variations in temperature, pressure, and concentration affect the processes of evaporation and solution in the same manner as true chemical reactions, and the simplest illustrations of heterogeneous equilibrium are represented by such processes. When a solid substance is brought into contact with a liquid, it continues to dissolve until the solution is saturated;— that is, until the ratio between the concentration of the substance in the liquid and solid phases has attained a fixed value. If the solid phase is a pure substance, not a solid solution, its concentration depends on its density only, and is constant, and therefore the solubility of such a substance is constant if the temperature and pressure are constant. Hence, the general expression for the equilibrium constant can be reduced to

$$K = C,$$

in which  $C$  represents the concentration of the soluble substance in the saturated solution. A similar expression represents the equilibrium between a liquid, or a solid, and its vapor. If the liquid or solid is pure, the concentration of the vapor in the vapor phase is constant. Heterogeneous equilibria, in which the concentrations of several reagents are concerned, involve reactions within each of the phases which make up the system and reactions between the phases. Further details relating to such equilibria will be discussed in Chapters VI and X.

## II. Equilibria Involving Electrolytes

**Preliminary Statements.** The reaction used to illustrate the general principles which determine chemical equilibrium, in the preceding section, did not involve electrolytic dissociation. Since these principles are universally valid, and since the most important quantitative processes involve reactions between electrolytes, it will be necessary to discuss in some detail the different types of equilibria between electrolytes.

When solutions containing different electrolytes are brought together, several different kinds of change become possible. Certain positive ions, having a strong affinity for electrons, will acquire one or more electrons, and become more stable entities, as neutral molecules or as positive ions of less net charge. In like manner, certain negative ions, having a strong tendency to give up electrons, will lose one or more electrons, reverting to the more stable state of neutral molecules or of negative ions of less net charge. Whenever there is an interchange of electrons, the acquiring bodies must gain as many electrons as the yielding bodies lose, since the solution as a whole is electrically neutral. This interchange of electrons may be accompanied by the breaking up of complex or polyatomic ions or by the formation of simple bodies into complex or polyatomic ions. All equations used to represent reactions involving ions in solution, then, must show an equality between the algebraic sum of the plus and minus charges associated with the ions on one side of the equation with those on the other side.



**Dissociation of Weak Acids and Bases.** The degree of dissociation of an electrolyte, that is, the ratio between the concentrations of the dissociated and undissociated forms of the electrolyte, is usually determined by comparing the electrical conductance of the electrolyte at the given concentration with the conductance of the same electrolyte at "infinite dilution," which is usually the dilution at which the degree of dissociation is not changed by further dilution. The method assumes that conductance is dependent upon the concentration of the dissociated electrolyte and the mobility of the ions in solution. When this method of measuring dissociation is used to determine the dissociation of weak electrolytes it is found that they obey the mass-law. The dissociation of a weak mono-basic acid HA should accord with the expression

$$(\text{HA}) \cdot k = (\text{H}^+) \cdot (\text{A}^-) \quad \text{or} \quad k = (\text{H}^+) \cdot (\text{A}^-) \div (\text{HA}),$$

in which is the dissociation constant of the acid in question. If its value has been determined, the concentration of  $\text{H}^+$ ,  $\text{A}^-$ , or HA in any solution in which the total concentration of the acid is known is easily calculated. The exact method of making the calculation is similar to that used in the calculation on page 60, but a simpler method which is accurate enough for many purposes is here advantageous. This method assumes that the dissociation constant of the acid is very small, and, since this is true of all weak acids, the error in assuming that (HA) equals the total concentration of electrolyte in the preceding expression is small. If  $x$  is used to represent  $(\text{H}^+)$ , it must also represent  $(\text{A}^-)$ , and if  $a$  represents the total concentration the expression becomes

$$ak = (x)(x) \quad \text{and} \quad (\text{H}^+) = (\text{A}^-) = \sqrt{ak}.$$

If a somewhat greater degree of accuracy is demanded this result may be called a first approximation and a second approximation calculated by using  $a$  minus the value found for  $x$  in place of  $a$ .

By analogy, the concentrations of hydroxyl ion in solutions of weak bases can be calculated from the expression:

$$(\text{OH}^-) = \sqrt{ak}.$$

**Dissociation of Strong Acids, Strong Bases, and Salts.** The large mass of data relating to the conductance of electrolytes, now available, shows that these substances can be divided into two well-defined groups. The first includes the weak acids and bases, whose change in degree of dissociation with varying concentration is in accord with the requirements of the mass-law, and whose dissociation constants are in all cases very small numbers. The second includes strong acids, strong bases and nearly all salts, which are very largely dissociated but whose degree of dissociation, as determined by conductance methods, does not vary with the dilution as required by the mass-law. The values found for 0.1 molal solution of electrolytes of the same type are similar, and it is sometimes assumed that all of these electrolytes which yield two univalent ions are 85 per cent dissociated, that those which yield one di- and two univalent ions are 75 per cent dissociated, and that those which yield two divalent ions are 50 per cent dissociated. Another assumption sometimes made in rough calculations is that the dissociation constant of electrolytes which yield two univalent ions is at least as great as one.

The degree of dissociation can also be calculated by the use of other methods, such as the lowering of the freezing point of aqueous solutions and electromotive force measurements, as will be explained in subsequent chapters. The results obtained by these methods usually differ considerably from those obtained by conductance measurements. The latter method assumes that the conductance is directly proportional to the concentration of the dissociated electrolyte, but it seems reasonable to assume that all the ions in the solution are surrounded by an electric field and exercise an attractive or repulsive force on each other and therefore affect each other's movements. If so, the conductance should not change in proportion as the total concentration changes, and this effect should be large in proportion as the total concentration of the ions in solution is large, and should be greater for di- and trivalent than for univalent ions. These suggestions are in accord with the data of a large amount of experimental work.

**The Activity Coefficient.** It is now generally believed that the determination of ionic concentrations by means of freezing-point lowering or electromotive force measurements defines the actual

effective concentration or "activity" of the ion concerned, which, in dilute solutions is usually less than the total concentration, and should be used in place of the total concentration in all calculations in which equilibrium relations are concerned. The ratio between the actual or effective concentration and the total concentration of the electrolyte from which the ion is derived is known as the "activity coefficient." Obviously this should be used instead of the degree of dissociation in ascertaining the effective concentration of the ions. It is also generally believed that all so-called strong electrolytes are completely dissociated. If so, the activity coefficient can also be defined as the ratio between the effective concentration and the total concentration of the ion in solution. Debye and Hückel<sup>1</sup> have formulated an expression showing the relation between the activity coefficient and the total concentration, which is based upon the two assumptions already stated, namely, first, that the dissociation of all strong electrolytes is complete; and second, all the ions in the solution exercise a restraining effect upon the ion whose activity is being measured. This expression takes into account the total concentration, the temperature, the number of charges on the ion, and the dielectric constant of the solvent.

The available data relating to activity coefficients are as yet meager and it is scarcely possible to ascertain the activity coefficients of more than a very limited number of the more common ions. For the present, in this book, we will be satisfied with first approximations in all calculations of equilibrium relations in which strong electrolytes are concerned, and we will disregard the difference between the actual and the effective concentrations of the ions.

**Dissociation in Solutions Containing Two Electrolytes which Yield a Common Ion.** The addition of a strong electrolyte to a solution of a weak electrolyte should affect the degree of dissociation of the latter if both electrolytes yield a common ion. This is a necessary consequence of the fact that the strong electrolyte must increase the concentration of the common ion and therefore necessitates some readjustment of the equilibrium. Assuming

<sup>1</sup> Debye and Hückel, *Physik. Zeit.*, 24, 185 (1923).

that the strong electrolyte is completely dissociated, the only readjustment which can take place is a decrease in the degree of dissociation of the weak electrolyte. The actual change can be easily calculated if the dissociation constant of the weak electrolyte and the concentrations of both electrolytes, are known. If, for example, the dissociation constant of the weak electrolyte, HA, is  $k_{\text{HA}}$ , its concentration is  $a$ , and the concentration of the strong electrolyte, RA, is  $b$ , and if we assume that the fraction of HA which remains dissociated is  $x$ , then

$$(\text{H}^+) = ax; (\text{A}^-) = b + ax; \text{ and } (\text{HA}) = a - ax.$$

Hence,

$$\frac{(ax)(b + ax)}{a - ax} = k_{\text{HA}}, \text{ and } a^2x^2 + ax(b + k_{\text{HA}}) = ak_{\text{HA}}.$$

This quadratic equation is easily solved, but since  $k$  is small,  $ax$  must be small as compared with  $a$  and  $b$ , and a satisfactory approximation may be made by using the simplified expression

$$\frac{(ax)b}{a} = k_{\text{HA}} \text{ or } ax = \frac{a}{b}k_{\text{HA}}.$$

If both electrolytes are weak the stronger should repress the ionization of the weaker provided its concentration is not too small as compared with that of the weaker, but the calculation of the changes which result when such electrolytes are mixed is not easily made. Let us assume that the total concentration of HA is  $a$ , its dissociation constant  $K_{\text{HA}}$ , and its degree of dissociation  $x$ ; and also that the total concentration of  $\text{HA}_1$  is  $b$ , its dissociation constant  $k_{\text{HA}_1}$ , and its degree of dissociation  $y$ . After equilibrium has been attained in the mixture, the following relations must be true:

$$(1) \quad k_{\text{HA}} = \frac{ax(ax + by)}{a(1 - x)} = \frac{x}{1 - x}(ax + by),$$

$$(2) \quad k_{\text{HA}_1} = \frac{by(ax + by)}{b(1 - y)} = \frac{y}{1 - y}(ax + by).$$

Dividing (1) by (2) we get

$$\frac{x}{1-x} \div \frac{y}{1-y} = k_{\text{HA}} \div k_{\text{HA}_1}.$$

That is, the ratio of the dissociated to undissociated HA bears the same relation to the ratio of dissociated to undissociated  $\text{HA}_1$  as the dissociation constant of HA bears to that of  $\text{HA}_1$ . This does not lead to a solution of  $x$  and  $y$  except by the method of trial and error. It will be recognized however that  $k_{\text{HA}} \div k_{\text{HA}_1}$  is a numerical expression of the tendency for the reaction to take place and has the properties of an equilibrium constant.

**Reactions Involving Displacement.** It will be recognized that  $\frac{x}{1-x} \div \frac{y}{1-y}$  of the preceding formula expresses the extent to which one electrolyte represses the ionization of another which yields the same ion. This is the essential feature of a large number of reactions which are frequently used in quantitative analysis. They include "displacement" of a weak acid from one of its salts by a strong acid, or of a weak base from one of its salts by a strong base. The reaction between a salt of the weak acid, HA, and a strong acid,  $\text{HA}_1$  is expressed by



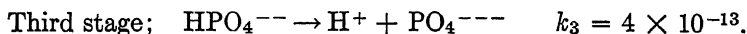
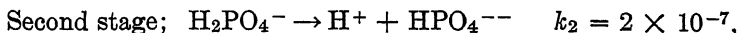
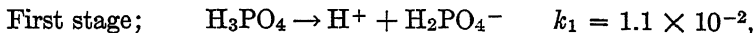
or

$$K = \frac{(\text{HA})(\text{A}_1^-)}{(\text{HA}_1)(\text{A}^-)}.$$

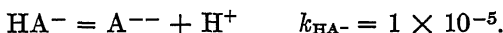
The expression on the right of the sign of equality represents  $\frac{x}{1-x} \div \frac{y}{1-y}$  and therefore  $K$  must equal  $k_{\text{HA}_1} \div k_{\text{HA}}$ . If the dissociation constants of the two acids are known, the equilibrium constant which determines the completeness of the entire process is easily calculated. The same result can be arrived at directly by dividing the equation for the dissociation constant of the strong acid by that for the dissociation constant of the weak acid.

**Dissociation of Electrolytes which Yield Two or More Univalent Ions of the Same Composition.** The dissociation of such elec-

trolytes takes place in stages and the constants which determine each stage of the process decrease in value rapidly at each stage of the dissociation. For example, phosphoric acid dissociates as follows:



Since each stage of the dissociation yields a common ion, each step in the process must repress the stage which follows it. Since  $k_1$  exceeds  $k_2$  and  $k_2$  exceeds  $k_3$  by such large differences, the dissociation due to the second as compared to the first and of the third as compared to the first and second can be neglected in most calculations. The value of  $(\text{H}^+)$  in a solution containing  $\alpha$  moles of  $\text{H}_3\text{PO}_4$  per liter is practically that of a monobasic acid whose dissociation constant is  $1.1 \times 10^{-2}$  and whose concentration is  $\alpha$ . If smaller differences exist between the different constants, and if the total concentration is small, it may be necessary to consider the second and third stages. For example, if we have



and if the total concentration is  $1 \times 10^{-3}$ , then  $(\text{H}^+)$  for the first stage is

$$\sqrt{(1 \times 10^{-4})(1 \times 10^{-3})} = 3.16 \times 10^{-4}.$$

In considering the second stage it will be recognized that  $(\text{H}^+)$  from the first stage equals  $(\text{HA}^-)$  and owing to the smaller value of  $k_{\text{HA}^-}$  both  $(\text{H}^+)$  and  $(\text{HA}^-)$  must be large as compared with  $(\text{H}^+)$ , resulting from the dissociation of  $\text{HA}^-$ . Hence,

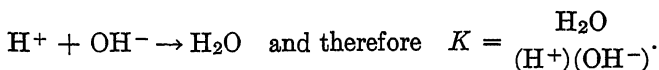
$$k_{\text{HA}^-} = \frac{(\text{H}^+)(\text{A}^{--})}{(\text{HA}^-)} \text{ becomes simply } k_{\text{HA}^-} = (\text{A}^{--}).$$

Since  $(\text{H}^+)$  resulting from the second stage equals  $(\text{A}^{--})$  whose

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value is  $1 \times 10^{-5}$ , the total value of  $(H^+)$  becomes  $3.16 \times 10^{-4} + 1 \times 10^{-5} = 3.26 \times 10^{-4}$ .

**Reactions Involving Neutralization.** These reactions are represented by the expression:



Although this represents the reverse of the ionization of water it differs from the dissociation equilibria heretofore considered because water is also the solvent and is present in such large amounts as compared with the  $H^+$  and  $OH^-$  that the water formed or used up during the progress of the reaction has a negligible effect upon the total concentration. This justifies assigning a constant value to  $(H_2O)$  in all such equilibria, and assuming that the product  $(H^+) \times (OH^-)$  also has a constant value. If  $(H_2O)$  is given a value of one,  $K$  must equal the reciprocal of  $(H^+) \times (OH^-)$ . The ion product of water,  $(H^+) \times (OH^-)$ , has been determined by a number of methods and is found to vary from  $1 \times 10^{-14.23}$  at  $18^\circ C$ . to  $1 \times 10^{-12.23}$  at  $100^\circ C$ . At ordinary working temperatures the value  $1 \times 10^{-14}$  may be used, and this will be employed throughout this book.

One consequence of this relation is that in any aqueous solution in which  $(H^+)$  is known  $(OH^-)$  can be found by dividing  $1 \times 10^{-14}$  by the value of  $(H^+)$ . In a similar manner,  $(H^+)$  can be found if  $(OH^-)$  is known. This also enables us to define a neutral solution as one in which  $H^+$  and  $OH^-$  have the same value as in pure water, which is obviously  $\sqrt{1 \times 10^{-14}}$  or  $1 \times 10^{-7}$ .

A second consequence of this relation is that the equilibrium constant of a reaction between an acid and a base, both of which are completely dissociated, has the value  $1 \times 10^{14}$ ; it may be assumed that this is true of all reactions between strong acids and strong bases. If either acid or base, and especially if both acid and base are weak, the value of the constant is less. The equilibrium constant of such a reaction is expressed by

$$K_{(\text{neutralization})} = \frac{(R^+)(A^-)}{(ROH)(HA)}.$$

In any mixture of the acid and base three conditions must be satisfied, namely,

$$(1) \quad k_a = \frac{(H^+)(A^-)}{(HA)},$$

$$(2) \quad k_b = \frac{(OH^-)(R^+)}{(ROH)},$$

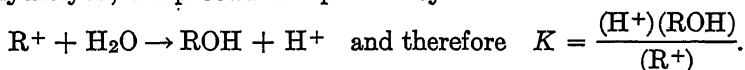
$$(3) \quad k_{H_2O} = (H^+)(OH^-)$$

If we multiply (1) by (2) and divide by (3) we obtain

$$\frac{k_a \cdot k_b}{k_{H_2O}} = \frac{(A^-)}{(HA)} \cdot \frac{(R^+)}{(ROH)}.$$

Since the expression on the left of the sign of equality in the last equation is identical with that on the left in the expression for neutralization  $\frac{k_a \cdot k_b}{k_{H_2O}}$  must equal  $K$ . Hence the completeness of such reactions is large in proportion as the dissociation constant of the acid and base concerned is large.

**Reactions Involving Hydrolysis.** The hydrolysis of a salt represents the reverse of the process which takes place when an acid neutralizes a base. In the most general case, both anion and cation undergo hydrolysis, the anion forming undissociated acid and the cation undissociated base, and the "hydrolysis constant" is the reciprocal of the neutralization constant. This hydrolysis constant can therefore be calculated from the dissociation constant of the acid and base formed and the ion product of water. In other cases, only one of the two ions undergoes hydrolysis. This simplifies the procedure for the calculation of the composition of the solution at equilibrium. If  $R^+$  is a cation which undergoes hydrolysis, the process is expressed by



There are two requirements which must be satisfied in such equilibria, namely,

$$(1) \quad \frac{(R^+)(OH^-)}{(ROH)} = k_b \quad \text{and} \quad (2) \quad (H^+)(OH^-) = k_{H_2O}.$$



If we divide (2) by (1) we obtain

$$\frac{(\text{H}^+)(\text{OH}^-)}{1} \cdot \frac{(\text{ROH})}{(\text{R}^+)(\text{OH}^-)} = \frac{k_{\text{H}_2\text{O}}}{k_b} = K.$$

It is obvious that  $K$  of this expression is identical with the hydrolysis constant and its value may be calculated by dividing the ion product of water by the dissociation constant of the base. If it is assumed that the salt is completely dissociated, that the anion is not appreciably hydrolyzed, that  $a$  represents the total concentration of the salt, and  $x$  is the hydrogen ion concentration, then

$$(\text{H}^+) = (\text{ROH}) = x \quad \text{and} \quad (\text{R}^+) = (a - x),$$

and therefore

$$(a - x)K_{\text{hydrolysis}} = (x)(x) \quad \text{and} \quad x = \sqrt{K_{\text{hydrolysis}}(a - x)}.$$

If  $x$  is small compared with  $a$ , which is usually true, then

$$x = \sqrt{a \cdot K_{\text{hydrolysis}}}.$$

The value of  $(\text{H}^+)$  in a 0.1 molal solution of ammonium chloride becomes

$$\sqrt{0.1(1 \times 10^{-14} \div 1.8 \times 10^{-5})} \quad \text{or} \quad 7.4 \times 10^{-6}.$$

Similarly if the anion is hydrolyzed and the cation is not, and  $x$  represents  $(\text{OH}^-)$ , the corresponding expression which is deduced in the same manner, becomes

$$x = (\text{OH}^-) = \sqrt{a(k_{\text{H}_2\text{O}} \div k_{\text{acid}})}.$$

Owing to the very small value of  $k_{\text{H}_2\text{O}}$ , the amount of hydrolysis is not appreciable unless the dissociation constant of the acid or base formed by hydrolysis is very small. Those ions which are appreciably hydrolyzed are commonly designated "weak" ions.

The salts of dibasic acids hydrolyze in stages, the constant for

the first stage being determined by the constant which determines the second stage of the dissociation of the acid formed. The second stage of the process, which is determined by the first dissociation constant of the acid, is relatively unimportant and is usually disregarded.

**A Table of Dissociation Constants.** The preceding paragraphs of this chapter suggest some of the uses which can be made of the dissociation constants of acids and bases. Several compilations of such data have been made.<sup>1</sup> Table I, which is compiled from a variety of sources gives values for some of the more important acids and bases only.

**The Meaning and Use of  $P_H$  Values.** The very small magnitudes used in the equilibrium calculations just considered may be more conveniently expressed by the device first suggested by Sorensen to express small values of  $(H^+)$ . This consists in using the common logarithm of the number with its sign changed, which is then designated by the symbol  $P_H$ , instead of by the number itself. According to this device the  $P_H$  of a solution in which  $(H^+)$  equals  $1 \times 10^{-8}$  becomes  $-\log(1 \times 10^{-8})$  or  $\log 10^8$ , and hence  $P_H = 8$ .

If the number concerned involves a multiple of some power of ten the conversion of it to the corresponding  $P_H$  value requires that the logarithm of this multiple be combined with that of the power of ten. Thus, the  $P_H$  value of  $3.4 \times 10^{-8}$  becomes  $-(\log 3.4 + \log 10^{-8})$ , or  $-(.53 - 8)$  which is 7.47.

The conversion of  $P_H$  values to the corresponding numbers requires the reverse of the process. Thus, a  $P_H$  value of 7.47 gives a number which corresponds to the  $\log [+8 + (-.53)] \times -1$ , or  $3.4 \times 10^{-8}$ . The same scheme may be used of course to represent small concentrations of other ions. It will be recognized that adding two  $P_H$  values would represent multiplication of the two numbers to which they correspond and subtracting to dividing one by the other.

**The Meaning and Use of Free Energy Data.** It is a well-known fact that a definite amount of heat is either liberated or absorbed when a definite chemical change takes place. This indicates that

<sup>1</sup> One of the most complete is to be found in the volume entitled "Indicator's" by Kolthoff and Furman (1926), page 249.

TABLE I  
DISSOCIATION CONSTANTS OF VARIOUS COMPOUNDS  
A. Inorganic Acids

			$k_1$	$k_2$	$k_3$
Arsenic.....	$H_3AsO_4$	25° C.	$5.0 \times 10^{-3}$		
Arsenious.....	$H_2AsO_3$	25°	$6.0 \times 10^{-10}$		
Boric.....	$HBO_2$	18°	$1.7 \times 10^{-9}$		
Carbonic.....	$H_2CO_3$	18°	$3.0 \times 10^{-7}$	$6.00 \times 10^{-11}$	
Hydrosulfuric.....	$H_2S$	18°	$5.7 \times 10^{-8}$	$1.2 \times 10^{-15}$	
Nitrous.....	$HNO_2$	25°	$4.0 \times 10^{-4}$		
Orthophosphoric.....	$H_3PO_4$	25°	$1.1 \times 10^{-2}$	$1.95 \times 10^{-7}$	$3.6 \times 10^{-13}$
*Pyrophosphoric.....	$H_4P_2O_7$	25°	$1.4 \times 10^{-1}$	$1.10 \times 10^{-2}$	$2.9 \times 10^{-7}$
Sulfuric.....	$H_2SO_4$	25°		$1.70 \times 10^{-2}$	
Sulfurous.....	$H_2SO_3$	18°	$1.7 \times 10^{-2}$	$1.00 \times 10^{-7}$	

\*  $k_4 = 3.6 \times 10^{-9}$ .

B. Organic Acids

Acetic.....	$CH_3 \cdot COOH$	18° C.	$1.8 \times 10^{-5}$		
Benzoic.....	$C_6H_5 \cdot COOH$	25°	$6.86 \times 10^{-5}$		
Carbolic.....	$C_6H_5 \cdot OH$	25°	$1.3 \times 10^{-10}$		

Cinnamic.....	$C_6H_5 \cdot CH : CH \cdot COOH$	25°	$3.68 \times 10^{-5}$	$5.00 \times 10^{-5}$	$1.8 \times 10^{-6}$
Citric.....	$C_6H_4 \cdot HO \cdot (COOH)_3$	25°	$8.2 \times 10^{-4}$		
Formic.....	$H \cdot COOH$	18°	$2.00 \times 10^{-4}$		
Hydrocyanic.....	$HCN$	25°	$7.20 \times 10^{-10}$		
Malic.....	$CH_3 \cdot CHOH \cdot (COOH)_2$	25°	$4.00 \times 10^{-4}$		
Oxalic.....	$(COOH)_2$	25°	$3.80 \times 10^{-2}$	$*3.50 \times 10^{-5}$	
Picric.....	$C_6H_3(NO_2)_3OH$	25°	$1.60 \times 10^{-1}$		
Salicylic.....	$C_6H_4 \cdot OH \cdot COOH$	25°	$1.06 \times 10^{-3}$		
Succinic.....	$C_2H_4(COOH)_2$	25°	$6.55 \times 10^{-5}$	$5.90 \times 10^{-6}$	
Tartaric.....	$C_2H_2(COOH)_2(HO)_2$	25°	$1.00 \times 10^{-3}$	$*5.00 \times 10^{-5}$	
Trichlor acetic.....	$CCl_3(COOH)$	18°	$1.30 \times 10^{-1}$		

## C. Bases

Aniline.....	$C_6H_5 \cdot NH_2$	25° C.	$3.50 \times 10^{-10}$		
Hydrazine.....	$(NH_2)_2$	25° C.	$2.00 \times 10^{-6}$		
Methyl amine.....	$CH_3(NH_2)$	18°	$4.00 \times 10^{-4}$		
Ammonium hydroxide.....	$(NH_4)OH$	25°	$1.80 \times 10^{-5}$		
Dimethyl amine.....	$(CH_3)_2NH$	25°	$5.50 \times 10^{-4}$		
Trimethyl amine.....	$(CH_3)_3N$	25°	$6.50 \times 10^{-5}$		
Pyridine.....	$C_6H_5N$	25°	$2.30 \times 10^{-8}$		

\* At 18° instead of 25°.

changes in the energy content of the system must be associated with changes in the concentrations of the reagents which the system contains. It is also possible to make certain reactions take place in such a manner as to yield mechanical energy. This is true when electrical energy is obtained by causing a reaction to take place in a galvanic cell. The maximum amount of mechanical energy which is rendered available when such a change takes place is found to be a fixed magnitude, which is characteristic of the reaction concerned, and is in no way related to the heat change associated with the same reaction. This magnitude is believed to be a true measure of the force which causes the reaction to take place and is known as the "Free Energy" of the reaction. It can be thought of as the difference between the sum of the free energies associated with the original and the resultant substances. This difference must have a negative value, that is, the system must lose free energy, if the process takes place spontaneously. The difference must be zero if the system is at equilibrium. Since these changes ultimately represent increases in the concentrations of certain reagents and decreases in the concentrations of others the intensity factor of the free energy change must be closely related to the equilibrium constant. If it be assumed that the amount of change concerned is that associated with the quantities represented by the equation used to express the reaction, the relation between the free energy and the equilibrium constant corresponds to the expression;

$$-\Delta F = RT \ln K,$$

in which  $\Delta F$  is the free energy expressed in calories,  $R$  is the gas constant, 1.995, expressed in calories,  $T$  is the absolute temperature, and  $K$  is the equilibrium constant as defined on page 58. Using the factor 2.303 to change natural to common logarithms we have, at 25° C.,

$$-\Delta F = 1.995 \times 298 \times 2.303 \log K = 1365 \log K.$$

We have seen that the equilibrium constant for the reaction

## FACTORS DETERMINING CHEMICAL EQUILIBRIUM 77

between a strong acid and a strong base is  $1 \times 10^{14}$ , therefore for all such reactions

$$-\Delta F = 1365 \times 14 = 19,110 \text{ calories.}$$

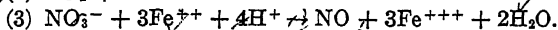
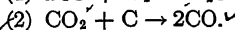
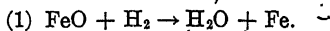
This means that the attainment of equilibrium between one mole of  $\text{OH}^-$  and one of  $\text{H}^+$ , both at molal concentrations at the outset, is capable of yielding mechanical energy corresponding to this number of calories, or that the amount of mechanical energy needed to prevent the reaction from taking place is 19,110 calories.

It is also clear that if  $\Delta F$  is known, it is an easy task to calculate  $K$ , and since free energy equations can be added or subtracted it is possible to calculate  $K$  for many reactions which cannot be determined by direct measurement. Tables giving the free energies of most of the more common reagents have been prepared and it is possible to use them to ascertain the equilibrium constants of many reactions for which direct experimental data are lacking.

### Questions and Problems. Series 4

1. Give the composition of the phases present in mixtures obtained by adding (a) alcohol and barium carbonate to water, (b) kerosene and sodium chloride in large excess to water.

2. Explain why the following equilibria would or would not be affected by changes in pressure:



3. If the equilibrium constant of the reaction between acetic acid and alcohol (see page 60) had the value (a) 40, or (b) 0.4 instead of 4, what weights of ethyl acetate and water would be formed when 240 grams of acetic acid are mixed with 138 grams of alcohol?

Ans. (a) 248.9 and 50.8, (b) 117.5 and 24.03.

4. The dissociation constant of a certain monobasic acid is  $1 \times 10^{-4}$ . Calculate  $(\text{H}^+)$  in a solution in which the total concentration is 1 molal by (a) the approximate and (b) the exact method. Ans. (a) .01, (b) 0.00995.

5. Plot curves in which ordinates represent  $(\text{H}^+)$  and abscissas total concentration of  $\text{HCl}$  in solutions varying from 0.001 to 1 molal, assuming (a) dissociation is complete at all concentrations, (b) the dissociation constant of hydrochloric acid is 1. Add a third curve for "effective" concentration of  $\text{H}^+$  assuming that the activity coefficients (see page 65) of  $\text{HCl}$  are 0.990 at

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0.001M, 0.855 at 0.05M, 0.823 at 0.1M, 0.783 at 0.3M, 0.773 at 0.5M, 0.789 at 0.7M and 0.829 at M.

✓ 6. Calculate  $(\text{OH}^+)$  in a solution composed of 100 cc. of water, 100 cc. of 6N ammonium hydroxide and 5 grams of ammonium chloride.

*Ans.* 0.00012.

✓ 7. Calculate the neutralization constants for the reactions between (a) ammonium hydroxide and hydrochloric acid, (b) ammonium hydroxide and benzoic acid, (c) sodium hydroxide and nitrous acid.

✓ 8. Calculate the hydrolysis constants for the reactions between water and (a) sodium borate, (b) potassium sulfite, (c) ammonium cyanide.

✓ 9. Calculate the  $P_H$  values corresponding to  $(\text{H}^+) =$  (a)  $7.1 \times 10^{-3}$ , (b)  $3.8 \times 10^{-3}$ . Calculate  $(\text{H}^+)$  corresponding to  $P_H$ , (c) 4.72, (d) 7.16.

*Ans.* (a) 2.15, (b) 7.42, (c)  $1.9 \times 10^{-5}$ , (d)  $6.9 \times 10^{-8}$ .

## SECTION II

### GAS EVOLUTION PROCESSES

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#### CHAPTER VI

#### GENERAL FEATURES OF GAS EVOLUTION PROCESSES

**The Decomposition of Carbonates.** The simplest examples of this class of determinations are those in which the formation of a gaseous product is effected by a change in temperature. The determinations of carbon dioxide in certain carbonates and of water in certain hydrates furnish good illustrations. The decomposition of calcium carbonate is expressed by the reaction,



The system here represented consists of two solid phases, each of which is a pure substance and therefore has a constant concentration, and a gas phase the composition of which may vary. Although the vapor pressures of calcium oxide and calcium carbonate, within the range of temperatures usually employed in analytical work, are too small to be easily measured, theoretically they must be thought of as being appreciably volatile, and hence the vapor phase which is in equilibrium with the two solids must contain both of these substances in addition to carbon dioxide. Since however their concentrations in the solid form are constant, their concentrations in the vapor phase with which they are in equilibrium must also be constant. The concentrations of calcium oxide and calcium carbonate in the gas phase can therefore be represented by  $k$  and  $k'$  respectively, as long as appreciable amounts of these solids are in contact with the gas phase. The expression for the equilibrium in the gas phase then becomes

$$k' \times K = k + (\text{CO}_2),$$



but the three constants may be combined into a single constant  $K'$  and the expression then becomes simply

$$K' = (\text{CO}_2).$$

In this expression  $K'$  is actually a multiple of the true equilibrium constant, but it possesses the essential properties of the true equilibrium constant and, unlike the latter, can be determined experimentally with but little difficulty. If a small amount of pure  $\text{CaCO}_3$  is placed in an evacuated tube, and the latter heated to a fixed temperature, the pressure in the tube gradually increases to a certain maximum value owing to decomposition of the carbonate. This pressure can be accurately measured by means of a mercury guage and from this measurement the total concentration of the three molecular species can be calculated; since, however, the partial pressures due to calcium oxide and calcium carbonate vapors are too small to be measured the pressure can be assumed to represent carbon dioxide only.

**Equilibrium Measured by Pressure.** Since equal volumes of all gases, when measured under the same conditions of pressure and temperature, contain the same number of molecules (Avogadro's Hypothesis), and since the pressure depends directly upon the number of molecules, the pressure of any gas must vary directly with the molal concentration. It is perfectly logical therefore to express the value of the equilibrium constant of the reaction under consideration in terms of pressure rather than of concentration. The equilibrium constant for the reaction representing the decomposition of calcium carbonate then becomes the maximum pressure resulting from the decomposition at the chosen temperature. It is sometimes spoken of as the "dissociation pressure." It may also be thought of as the escaping tendency or fugacity of the carbon dioxide or the intensity factor of the expression representing the amount of mechanical resistance which the reaction is able to equalize.

**Effect of Temperature upon the Equilibrium.** Since these reactions are all associated with an absorption of heat, an increase in temperature should increase the dissociation pressure (Theorem of Le Chatelier). The results of some measurements<sup>1</sup> of the

<sup>1</sup> Andrussov, *Zeit. physik. Chem.* 116, 95 (1925).

dissociation pressure of calcium carbonate at a number of temperatures are given in the form of a graph in Fig. 19. In this diagram all points below the graph represent conditions at which solid calcium oxide and the gas phase are in equilibrium, and all points above it represent those at which calcium carbonate and the gas phase are in equilibrium. Solid calcium oxide cannot exist as a stable phase at conditions corresponding to points above the graph, nor solid calcium carbonate at those represented by points below it. It should be noted that the pressure here concerned is that due to carbon dioxide only. If other gases such as oxygen or nitrogen are present, they must also exert a pressure, but the pressure due to them has only a negligible effect upon the equilibrium. Expressed differently, it is the *partial pressure* of the carbon dioxide in the gas phase which determines the equilibrium.

A quantitative expression for the relation between temperature and dissociation pressure of reactions of this type can be derived from the Clausius Clapeyron Equation,<sup>1</sup> namely,

$$\log p = (-Q \div T) + C,$$

<sup>1</sup> For derivation and use of this see any recent treatise on Theoretical Chemistry.

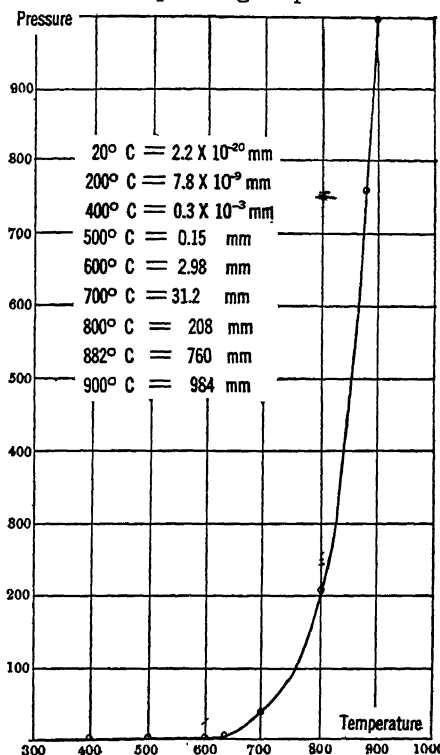


Fig. 19.—Curve representing dissociation pressure of calcium carbonate.

in which  $p$  is the dissociation pressure,  $Q$  is the heat absorbed by the reaction,  $T$  the absolute temperature, and  $C$  is a constant. The expression assumes that the heat absorbed is constant and also that the liberated gas behaves like a perfect gas; neither of these assumptions is correct although the errors which they introduce are usually negligible. Various empirical modifications, designed to represent this relation with greater accuracy have been used. The expression found to fit the data of Fig. 19 is,

$$\log p = (-8731 \div T) - 0.000866T + 1.75 \log T + 6.0808,$$

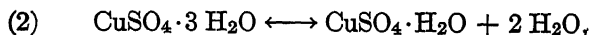
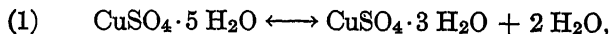
in which  $p$  is the pressure in millimeters of mercury. By use of this expression it can be calculated that calcium carbonate is stable in ordinary air which contains about 0.03 per cent of carbon dioxide, up to  $513^{\circ}\text{C}$ . It is also found that although precipitated calcium carbonate rapidly attains true equilibrium when heated, this is not true of naturally occurring samples. The latter can be heated to temperatures in excess of that named for several hours before appreciable decomposition occurs.

**The Dehydration of Salts.** A second illustration of this class of processes is found in the methods used for the determination of chemically combined water. Such determinations are based upon reversible processes represented by



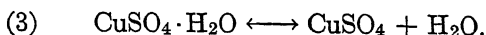
The equilibrium constant for such reactions can also be reduced to the expression  $K = C$  or  $K = p$ , in which  $C$  is the concentration and  $p$  is the pressure of the water vapor which is in equilibrium with the two solid phases.

Salts which are capable of forming a number of different hydrates may yield a number of equilibria in which any two of the possible solids, in addition to water vapor, are concerned. Cupric sulfate, for example, yields the solids  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . The equilibria represented by



have been measured and are represented graphically in Fig. 20.

Obviously complete dehydration would involve a third reaction represented by



Only a few points on the graph representing this equilibrium have been measured but it is almost certain that it lies entirely below that for (2). Still other equilibria are possible, namely;

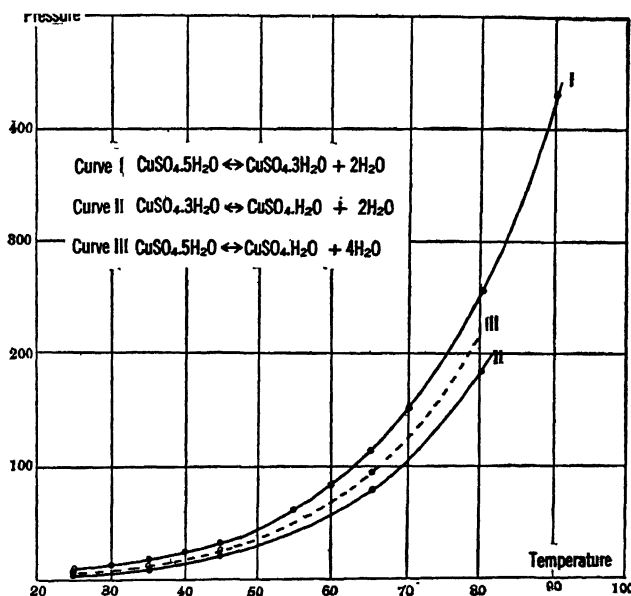
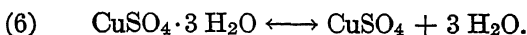
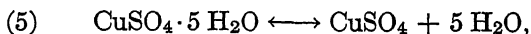
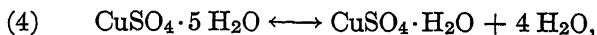


Fig. 20.—Curves representing the dissociation pressures of hydrates of cupric sulfate

It can be calculated that the graph for (4) lies between those for (1) and (2), as shown by the dotted line of Fig. 20, but further data are needed for the calculation of the graphs representing (5) and (6).

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Although it is probable that all of these reactions can be made to take place spontaneously, that is, with the loss of a certain amount of free energy, when one of the hydrates is maintained at the proper temperature and pressure, it is not possible to predict which of the various possible reactions will actually take place without data as to their respective rates. These rates are in no way dependent upon the values of the equilibrium constants. They are largely influenced by the presence of catalysts, especially the solids which are produced by the reactions actually taking place. The presence of even small amounts of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  increased the speed at which reaction (2) took place, and in general the presence of a certain solid may be expected to increase the speed of the reaction which yields that solid as a product. In such systems as this every pair of solids is stable within a certain range of pressure and temperature values, but equilibria in which one or both of these solids are "metastable" are also possible if the rate at which the change of the metastable to the stable solid is sufficiently low. Complete dehydration demands conditions represented by points on the pressure-temperature diagram lying below the undetermined points on the graphs representing equilibria (3), (5) and (6). The determination of water in a salt which yields a single hydrate only requires maintenance of conditions corresponding to points below the graph representing equilibria between hydrated and anhydrous salt. The presence of a small quantity of the anhydrous salt, and maintenance of much higher temperatures and lower pressures than those of the equilibrium, increases the speed at which dehydration takes place.

The conditions for the determination of water in salts which yield a number of hydrates are not so easily formulated. Actual experiments in which samples of pure hydrate are heated for definite periods of time under definite conditions are necessary before correct and rapid methods of procedure can be specified for such determinations.

✓ **Hydrates Which Form Liquid Phases.** Certain hydrates, such as  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  "melt," that is, form at specified temperatures liquids of the same composition as the solid salts. Others,

such as  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ,  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  form a liquid phase associated with a new solid phase, which is either a lower hydrate or an anhydrous salt. The liquid phase of the former group may be evaporated at or above the melting temperature, but this must finally yield a new solid phase which is also a lower hydrate or an anhydrous salt. The evaporation of such mixtures is troublesome owing to sputtering. Unless evaporated slowly mechanical losses make it impossible to find the weight of the residual salt with quantitative accuracy. In both groups the equilibrium is expressed by  $K = C$ , in which  $C$  is the concentration of water vapor of the gas phase in equilibrium with the liquid phase. If the liquid is associated with a solid, its concentration and therefore  $C$  is fixed by the temperature only; if no solid is present  $C$  varies with both temperature and concentration of the liquid.

**The Evolution Method.** The weight of gas liberated by such reactions as those under discussion can often be ascertained with a high degree of accuracy by determining the total loss in the weight of the apparatus in which the reaction is made to take place, that is by determining the weight of the liberated gas by the "evolution method." In general there are two extremes represented in the procedure adopted. In one the temperature is kept high and no attempt made to reduce the partial pressure of the escaping gas; in the other the temperature is kept lower and the partial pressure of the escaping gas is reduced artificially. If the sample is heated in an open crucible or a vessel of similar shape, the escaping gas accumulates, the air in the vessel is displaced by it, and the partial pressure of this gas increases until it reaches that of the atmosphere. Since it is the film of gaseous mixture in immediate contact with the solid which determines the equilibrium it is necessary to heat the sample to a temperature at which the dissociation pressure exceeds the pressure of the atmosphere to effect a complete reaction. Frequently a still higher temperature becomes necessary in order to make the reaction sufficiently rapid. In many determinations it is not possible to heat the sample to the necessary temperature without causing appreciable volatilization of some of the solid residue, or inducing other reactions to take place which also cause a change

in weight. It then becomes necessary to reduce the partial pressure of the liberated gas by passing a current of air or some simple gas over the sample which is being heated. This necessitates the use of a somewhat more elaborate apparatus similar to that used for the absorption method described in the next paragraph.

**The Absorption Method.** Since the residue left after heating the sample is often hygroscopic, and therefore difficult to weigh

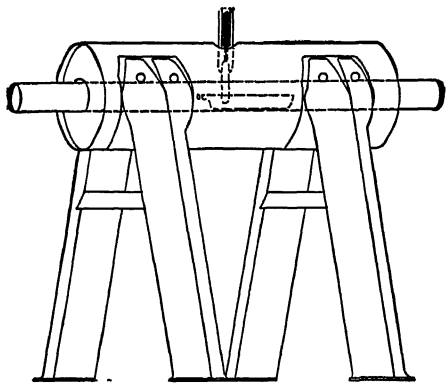


Fig. 21.—Muffle furnace for heating tubes.

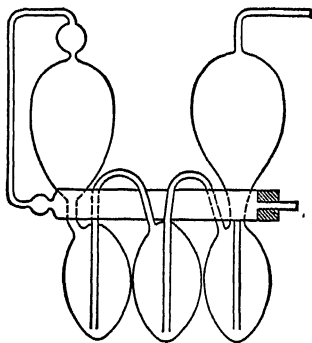


Fig. 22.—Geissler bulb.

accurately, and, since it is sometimes impossible to entirely suppress reactions involving changes in weight in addition to the one upon which the determination is based, it is often necessary to pass the liberated gas into an apparatus which absorbs it completely, and determine the weight by the direct or absorption method. The decomposition must then be made in a closed vessel and all the liberated gas washed through the absorbing system by means of a current of air or of a gas which is not taken up by the absorbing system. Such an apparatus is represented in Fig. 21. It consists of a glass tube supported horizontally in a cylindrical muffle, which is heated either by a flame or an electric current. The tube is large enough to retain a porcelain boat in which the sample to be analyzed is weighed out. The container for the reagent used to absorb the liberated gas should be so designed as to give the minimum weight and surface area

and at the same time permit of easy renewal of the reagent used. For solid absorbents a U-tube has the advantage of compactness and of distributing the reagent in a narrower column which is progressively exhausted as used, but it is somewhat troublesome to refill. Where large numbers of such determinations are being made a bottle-shaped vessel is generally used. For liquid absorbents a U-tube filled with pieces of ~~pumice stone~~ saturated with the liquid, or certain special forms of absorbent bulbs, such as the Geissler bulb of Fig. 22, are largely used.

**Theory of Absorption Processes.** The ability of an absorbing system to completely remove and retain one of the components of a mixed gas phase usually depends upon a chemical reaction. Such reactions must have a relatively large equilibrium constant and the conditions of absorption must be such as to make the reaction both complete and rapid. The reagents which are of especial importance are strongly basic substances such as mixtures of calcium ~~oxide~~ and sodium hydroxide, which are used for the absorption of acidic gases like hydrogen sulfide and carbon dioxide, and certain salts which are used for the absorption of water vapor. The action of the latter is simply the reverse of the process which takes place when hydrated salts are dehydrated, and it is obvious that only those salts which form hydrates whose dissociation pressures are very small, are satisfactory. A number of liquid and solid reagents comply with these requirements.

Phosphorous pentoxide is usually considered the most powerful dehydrating agent known, owing to the fact that the dissociation pressure of metaphosphoric acid is practically zero. As it is sold in the form of a fine white powder and the exposed surface rapidly becomes coated with a viscous liquid in which diffusion is slow it soon loses its efficiency. It is also an expensive reagent, and its use is avoided except when an unusual degree of dehydration is necessary.

The tetrahydrate of magnesium perchlorate rapidly takes up water vapor to form a hexahydrate whose dissociation pressure at room temperature seems to be about as low as that of metaphosphoric acid. It is to be had in the form of porous lumps and as the water absorbed on their surface rapidly penetrates into the interior it has a high percentage of efficiency. The



tests made with it seem to prove that it is as effective as phosphorous pentoxide.<sup>1</sup>

Calcium chloride forms a series of hydrates, all of which are extremely soluble. It may be obtained from dealers in two forms. The "fused salt" is almost anhydrous and is dense; the "granular" reagent, if fresh, contains from 12 to 20 per cent of water and is light and porous. Samples containing from 14 to 24 per cent of water yield a vapor pressure of 0.54 mm.; those containing from 24 to 40 per cent yield a pressure of 1.47 mm. and those containing from 40 to 50 per cent yield 2.47 mm. The fused salt acts more slowly than the lower hydrates.

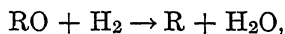
Concentrated sulfuric acid forms a series of liquid hydrates which are miscible with water in all proportions. The dissociation pressure of the concentrated acid is but little less than that of metaphosphoric acid, but increases rapidly with dilution. It has been measured for a wide range of concentrations at a small number of temperatures, and these data are very useful in preparing a dehydrating agent of definite power.

In using any of these dehydrating agents in a quantitative process it is evident that the absorbing tube, whose increase in weight is determined, must neither add to nor subtract from the water present in the large amount of air which must be passed through the apparatus. It is not necessary that the dehydration of the entering air be perfect, but it is necessary that it be dehydrated to the same degree as that effected by the tube which is weighed. This requirement is easily met by passing the entering air through a tube containing the same sample of dehydrating agent as is used in the tube whose increase in weight is determined. It should also be noted that hydration in both tubes takes place progressively, that is, the end at which the air enters gradually acquires the highest possible degree of hydration and ceases to be an effective absorbent. It is necessary therefore, in the repeated use of these tubes, always to attach the same end of both absorbing tubes to the tube in which the sample is heated.

**Evolution Processes in Which a Gaseous Reagent is Used.**  
Reactions in which one solid is completely transformed into

<sup>1</sup> Smith, Brown and Ross, Jour. Ind. Eng. Chem., 16, 20 (1924).

another as the result of the action of a gaseous reagent are frequently used in quantitative procedures. The amount of oxygen present in certain metallic oxides is easily ascertained by making use of reactions represented by

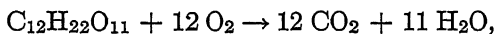


in which R represents a metal. Such reactions are usually reversible and, assuming that the concentrations of the solids are constant, the simplified form of the expression for the equilibrium constant becomes

$$K = (\text{H}_2\text{O}) \div (\text{H}_2).$$

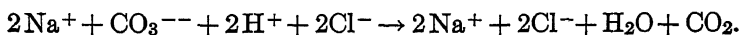
In such a reaction the value of  $K$  is not changed by substituting pressures for concentrations. If the sample is heated in a current of hydrogen the ratio of  $(\text{H}_2\text{O})$  to  $(\text{H}_2)$  can be made small, and if kept well below the equilibrium ratio should give rapid and complete conversion of the oxygen present into water. The oxygen can then be determined from the loss in weight of the sample used, or from the weight of water absorbed when the vapor phase is passed through a proper absorbing system.

Similarly the determination of carbon when present as solid carbon or of carbon and hydrogen in organic compounds can be effected by a "combustion process," that is by heating in a current of oxygen. Most of these reactions such as that represented by the equation



are not reversible processes but the rates at which they take place are increased and the tendency for the formation of intermediate oxidation products such as carbon monoxide, is reduced by keeping the concentration of oxygen large as compared with carbon dioxide and water vapor. Much ingenuity has been shown in developing special forms of apparatus in which such determinations can be carried out with speed and accuracy.

**Evolution Processes in Which a Liquid Reagent is Used.** A typical illustration of a gas evolution process based upon a reaction between a liquid and a solid is furnished by



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If we disregard the concentration of water, which in the solutions usually made use of remains nearly constant, the expression for the equilibrium in the liquid phase reduces to

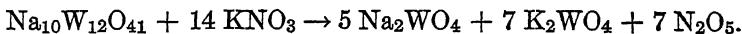
$$K = (\text{CO}_2) \div (\text{H}^+)^2.$$

It is evident that increasing  $(\text{H}^+)$  will increase greatly the completeness of the reaction because it appears in the denominator of the expression raised to the second power, also that decreasing  $(\text{CO}_2)$  will have a smaller effect. Since  $(\text{H}^+)$  may be made large by using more than the necessary amount of strong acid, and since  $(\text{CO}_2)$  may be reduced by warming the solution, no difficulty should be experienced in making such reactions practically complete. Most of them are also rapid.

The weight of the liberated gas can be determined by the evolution method, the absorption method, or by direct measurement of its volume. For the evolution method many special forms of apparatus, which are known as alkalimeters, can be employed. One of these is represented in Fig. 25, in which *A* is the receptacle which contains the substance to be analyzed and in which the reaction takes place, *B* the receptacle for the reagent used, and *C* the receptacle for the reagent used to dry the liberated gas. The weight of the entire apparatus as first charged with sample and reagents, and again after the reaction has been completed, is accurately determined; the difference gives the desired weight of the liberated gas.

**Evolution Processes in Which a Solid Reagent is Used.** Certain elements, such as silicon, tungsten, and boron, form oxides which are not appreciably volatile and which at higher temperatures are sufficiently acidic in their properties to displace certain of the weaker or more volatile acid anhydrides from their salts. The same type of reaction is effected by the acid salts of the anhydrides in question, such as sodium borate,  $\text{Na}_2\text{B}_4\text{O}_7$ , and sodium paratungstate,  $\text{Na}_{10}\text{W}_{12}\text{O}_{41}$ . The equilibria here concerned involve, at least in most cases, a partial fusion or sintering of the solids concerned. This is in fact essential for the completion of such reactions as it is almost impossible to assure perfect contact between the reagents concerned unless they finally yield a homogeneous liquid phase. As most salts are

miscible in all proportions in the liquid phase this requirement is easily complied with, provided the melting points of the salts are not too high. Aside from this feature their completeness depends for the most part upon the solubility of the liberated gas in the liquid formed. A typical illustration is furnished by the reaction between sodium paratungstate and potassium nitrate, which is represented by the equation:



The procedure for the use of such reactions in quantitative processes is extremely simple. It involves finding the loss in weight which results when a known amount of sample and of the proper reagent are both heated in a crucible.

### Questions and Problems, Series 5

✓ 1. Air is slowly passed through a wash bottle containing water and kept at 50° C.; if the partial pressure of the water vapor at that temperature is 92 mm., what weight of water should 1 liter of the saturated air contain assuming the temperature is 50° C., the total pressure 760 mm., and that water vapor behaves like a perfect gas?

Ans. 0.082 gram.

✓ 2. What are the partial pressures of water vapor, oxygen, and nitrogen in a mixture if the total pressure is 760 mm., and if 1 liter of the mixture contains 0.022 gram of water vapor, 0.8796 gram of nitrogen and 0.2665 gram of oxygen?

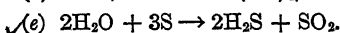
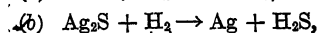
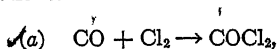
Ans. 22.6, 582.9, 154.4.

✓ 3. A mixture composed of equal volumes of carbon dioxide, nitrogen and oxygen is passed through a tube containing calcium oxide and calcium carbonate, which is kept at atmospheric pressure and 800° C. Predict from the data of Fig. 19 what changes, if any, should take place.

4. Assuming that the dissociation pressure of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  at 70° C. is 119.9 mm., what weight of  $\text{Na}_2\text{CO}_3$  will be found when 1 gram of this hydrate is placed in an evacuated flask which has a volume of 500 cc. and is heated to 70° C.?

Ans. 0.296 gram.

✓ 5. Give the simplest form of the expression for the equilibrium constants of the following reactions:



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6. Calculate the value of the equilibrium constant when expressed as a pressure relation for the reaction between carbon dioxide and carbon at  $850^{\circ}\text{C}$ ., assuming that the equilibrium mixture contains 6.23 per cent by volume of carbon dioxide and 93.77 per cent of carbon monoxide. *Ans.* 1411.

✓7. Write the equation representing the decomposition of silver oxide into silver and oxygen. Assuming that the dissociation pressure of the reaction, expressed in millimeters, is in agreement with the expression

$$\log p = (-2859 \div T) + 6.285,$$

calculate the temperature at which it is possible to completely decompose silver oxide when heated under atmospheric pressure without removal of liberated oxygen from the surface of the solid. *Ans.*  $567^{\circ}\text{C}$ .

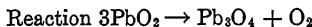
8. The dissociation pressure of a certain oxide at  $200^{\circ}\text{C}$ . is 400 mm.; calculate the value of  $K$ , expressed as a concentration. *Ans.* 0.01353.

✓9. An 800-cc. flask at  $25^{\circ}$  contains sufficient oxygen to produce a pressure of 800 mm. If one cc. of liquid water is introduced into the flask what pressure will exist inside the flask assuming that the vapor pressure of pure water at  $25^{\circ}$  is 23.42 mm.?

✓10. Calculate the percentage of  $\text{PbO}_2$  in a sample from the following data:

Weight of sample used for analysis..... 1.0324 gm.

Weight of sample after ignition..... 1.0011 gm.



## CHAPTER VII

### DETERMINATION OF WATER IN HYDRATED SALTS

#### I. General Properties of Hydrated Salts

**Purity of Salt Hydrates.** Solid salt hydrates of definite composition can be made to separate from supersaturated solutions, provided the solution does not contain appreciable concentrations of other salts which crystallize in the same form, and provided the vapor pressure of the solution is equal to or greater than that of the solid hydrate which separates at the same temperature. If a large degree of supersaturation is maintained, and coarse crystals are permitted to grow, these may occlude appreciable amounts of mother liquor and usually become sticky when crushed in a mortar. The separation of the crystals from the solution and the elimination of adhering mother liquor and hygroscopic moisture without partial dehydration is somewhat difficult to effect. If the salt is not very soluble the crystals are best separated on a coarse filter, washed as rapidly as possible with a small amount of water, and dried between folds of filter paper and by exposure in a thin layer to the air. If the crystals are very soluble, rapid washing with dilute alcohol and subsequent exposure to the air is more satisfactory. The proper treatment of every hydrate must be ascertained by experiment. Certain hydrates must be preserved at a low temperature and in tightly stoppered bottles if loss of combined water is to be prevented; such loss can usually be recognized by the dullness of the crystal surfaces and the presence of opaque masses of powdery material. Certain other hydrates absorb water and form saturated solutions even if kept in stoppered bottles. Such samples should be washed free from adhering solution with alcohol and the latter permitted to evaporate before being submitted to

analysis. A large number of hydrated salts which contain very nearly the theoretical percentage of water can be obtained from dealers.

**Dehydration by Direct Heating.** It was shown in the preceding chapter that several different equilibria may be concerned in the complete dehydration of a salt, and that the rates at which these equilibria are established largely determine the changes which actually take place when the hydrate is heated. Even where the dissociation pressures of these reactions are known, it is necessary to ascertain by actual experience the proper conditions for the rapid and complete dehydration of such salts. A large number of them can be made to lose the total amount of water present by heating in a current of dry air to  $300^{\circ}$ – $400^{\circ}$  C. These include  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$ ,  $\text{CrK}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  and  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ . This procedure does not give satisfactory dehydration with  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ .

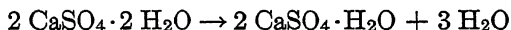
**Decomposition of Anhydrous Salts.** The thermal decomposition of anhydrous salts depends primarily upon the strength of the chemical forces holding the acidic and basic components in combination and upon the volatility of these components. The basic oxides are for the most part stable and but slightly volatile as compared with the anhydrides of sulfuric and nitric acid and of the elements of the halogen group. Hence, the various salts of any one of these acids should be stable in proportion as the basic properties of the basic constituent are strong. Many facts confirm this suggestion, although there are a number of exceptions. The sulfates of the sodium and calcium groups of metals are stable up to at least  $600^{\circ}$  C., and even the sulfate of copper does not begin to show appreciable decomposition up to  $400^{\circ}$  C. The nitrates, owing to the greater volatility of nitric oxide and nitrogen dioxide are less stable, but the nitrates of the alkalis can be heated to  $230^{\circ}$  C. with but little decomposition. The carbonates of the alkalis are perfectly stable up to about  $800^{\circ}$  C., and even calcium carbonate shows little dissociation up to  $600^{\circ}$  C. The chlorides, except those of most of the noble metals, are stable at  $350^{\circ}$  C., but at slightly higher temperatures many of

them begin to be appreciably volatile. Salts of ammonium are easily volatile and decompose at temperatures well below 300° C. This is true also of ammonium salts which are components of double salts.

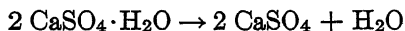
It should be noted also that the stability of a solid must depend to some extent upon the space relations of the component atoms or atomic groups in the space lattices. This probably explains some of the exceptions to the generalizations given.

## II. Determination of Water by Loss in Weight

**Behavior of Gypsum on Heating.** The composition of this mineral corresponds to the formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . It is frequently found in the form of colorless, transparent masses, which are practically free from other minerals and mechanically occluded impurities of all kinds, and which contain the theoretical percentage of water. It is chosen as a sample for the illustration of this method of determining water because it rapidly gives off all its water when heated in an open vessel to 250° C. and suffers no other change in weight than that due to the loss of water. When slowly heated in a loosely covered vessel, very little water is given off until a temperature of 102° C. is reached, and, if kept at this temperature for several days, only three-fourths of the water present is lost. The residue is composed of  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , which is the essential constituent of plaster of Paris. It is clear that at this temperature the dissociation pressure of the water vapor due to the reaction,



exceeds that of one atmosphere. If the temperature is still further increased to 160° C., the remainder of the water is driven off indicating that the dissociation pressure of the reaction,



also reaches that of one atmosphere. The rates at which these transformations take place at the temperatures named are very



low, and it is necessary to use a temperature of some 200° C. if it is desired to eliminate all of the water within a half hour. Since the only other reactions involving a change in weight, which can result from heating yield either calcium oxide, or a basic sulfate of calcium, and sulfur trioxide and, since these changes require a temperature of at least 600° C., there is no objection to expelling the water at a still higher temperature than 200° C.

**Properties of Anhydrous Calcium Sulfate.** Two forms of calcium sulfate are known. One of these, the so-called "soluble anhydrite," is formed when gypsum is heated to moderate temperatures only, and is both more soluble and much more hygroscopic than the other form, the "insoluble anhydrite." When gypsum is dehydrated below 500° C. difficulty is experienced in weighing the residual salt accurately owing to the speed with which it takes up water vapor from the air. This difficulty can be avoided by heating in a vessel which can be closed by means of a tightly-fitting stopper; and since ordinary glass does not begin to soften until a temperature of 400° C. is reached, a glass weighing bottle can be used for the determination, although it must be heated and allowed to cool slowly to prevent it from cracking. Satisfactory results can also be obtained by heating in a covered porcelain or platinum crucible, but some experience is necessary to weigh the residual salt with sufficient speed to prevent slight errors due to the absorption of water. The difficulty can also be avoided by using the absorption method, that is by collecting and weighing the liberated water, but this requires a more elaborate apparatus.

**Outline of Procedure.** Crush several grams of the air-dry sample in a clean mortar until the resulting particles are about the size of a pin head, and transfer to a clean dry "sample tube," that is a test tube about 1 cm. in diameter and 8 cm. long, which is provided with a good cork stopper. Procure a weighing bottle of not more than 20-cc. capacity, clean carefully, wipe both inner and outer surfaces with a dry cloth, and then allow to stand, preferably in the balance room, for twenty minutes. Weigh the bottle and cover accurately to within 0.5 mg. Remove the cover, add about 2 or 3 grams of the prepared sample, and again cover and weigh accurately to 0.2 mg.

Procure a nickel crucible of some 75-cc. capacity, cut a circular piece of wire gauze slightly larger than the bottom of the crucible, ignite it over a flame and place in the crucible as shown in Fig. 23. Cut a piece of asbestos cloth of slightly larger size and place on top of the gauze. Support the crucible on a piece of wire gauze which is placed some 2 inches above the top of a Bunsen burner, then remove the cover from the weighing bottle and place the bottle inside the crucible. Heat the gauze with a low flame for ten minutes, then gradually increase the heat until the wire gauze under the nickel muffle is heated to redness, and keep it at this temperature for a half hour, but do not permit the gas to take fire and burn over the gauze. The temperature attained inside the muffle should be about  $250^{\circ}\text{C}$ .

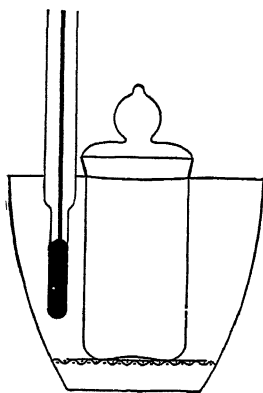


Fig. 23.—Apparatus for determination of water.

Shut off the gas, allow the muffle to cool for about three minutes, then place the cover in position, and transfer the bottle to a piece of paper, wood, or some other poor conductor of heat; allow to stand at or near the temperature of the balance room for twenty minutes. Weigh the bottle to within 0.2 mg.; if it shows any tendency to increase in weight while on the balance pan, allow to stand for another ten minutes and again weigh. Finally place the bottle in the muffle, heat as before for ten minutes, and again cool and weigh. If the difference between the two weighings does not exceed 0.3 mg. the dehydration of the sample can be assumed to be complete. Calculate the percentage of water present.

### ✓ III. Questions and Problems. Series 6

What is the error from buoyancy in this determination assuming that only platinum weights were used, and that the density in grams per cubic centimeter of platinum is 21.37, of gypsum is 2.32, of  $\text{CaSO}_4$  is 2.96 and of air is 0.0012?

*Ans.* 0.01 per cent.

## 98. FUNDAMENTALS OF QUANTITATIVE ANALYSIS

- ✓ 2. If you were to collect some of the liquid which is formed when the vapor given off by heating gypsum is condensed, how would you proceed in order to prove that it is pure water?
- ✓ 3. A sample of gypsum of the theoretical composition is found to contain 20.83 per cent of water; what is the percentage error? If the same degree of accuracy was attained in determining water in a hydrate containing 64.71 per cent of water, what result would be reported? *Ans.* 0.48 and 64.40.
- ✓ 4. A sample, composed of pure gypsum and a silicate which is not affected by heating to 300° C., is found to yield 8.84 per cent of water at this temperature; calculate the percentage of silicate present. *Ans.* 59.67.
- ✓ 5. If the sample of gypsum was associated with an easily decomposable carbonate, how could it be treated so as to liberate all the water but no carbon dioxide?
- ✓ 6. When a solution containing the sulfate ion is added to one containing calcium ion,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  usually separates; under what conditions would it be possible to cause  $\text{CaSO}_4$  to separate?
- ✓ 7. When 1 gram of a mixture composed of  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and a third non-volatile substance is heated in a narrow crucible for a long time at 950° C., it is found to lose 0.175 gram in weight. When the residue is heated to 1200° C. it loses 0.101 gram more. Assuming that the dissociation pressure of  $\text{CaCO}_3$  is 760 mm. at 900° C. and that of  $\text{SrCO}_3$  is 760 mm. at 1155° C. what percentages of these carbonates must be present? *Ans.* 39.77 and 33.88.

### ✓ IV. Determination of Water in Hydrated Salts by Absorption.

**Preparation of Sample.** The procedure outlined below applies to those hydrates which lose all their water rapidly when heated to between 350° and 400° C. in a current of dry air, and which do not yield appreciable amounts of any other volatile product which is retained by the absorption tube. In many cases the loss in weight of the sample heated can be used as a check on the weight of the water absorbed. The sample should be crushed to particles of about the size of a pin head and mixed in order to insure uniformity in its composition, but very fine crushing should be avoided as it has been shown that certain hydrates lose appreciable amounts of water when finely ground, probably owing to the heat developed by friction.

**Assembling and Charging Apparatus.** Set up an apparatus similar to that represented in Fig. 24, consisting of a 13-inch length of combustion tubing *A*; a Marchand tube *B*, which weighs about 40 grams when charged with granular calcium chlo-

ride; a drying tube *C*, charged with the same sample of calcium chloride as (*B*); a porcelain boat *D*; and an empty U-tube *E* of about the same surface area as *B*. Use tightly fitting rubber stoppers to attach *B* and *C* to *A*, and provide plugs with which to close the ends of *B*, *C* and *E*. Dry out *A* by heating the muffle with a bat's wing burner for some ten minutes, during which time about 1 liter of air should be drawn through the apparatus by means of the aspirator *F*. Shut off the gas, remove the boat from *A* with a wire hook, disconnect *B*, cover both ends with plugs, and allow *B* and *D* to stand in or near the balance room for twenty minutes. Close the open end of *A* with a stop-

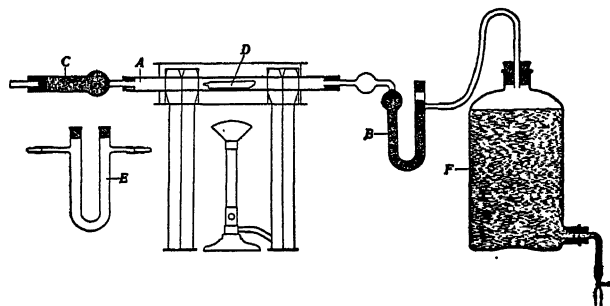


Fig. 24.—Apparatus for determination of water by absorption.

per. Weigh the boat, charge with sufficient sample to yield at least 0.4 gram of water, and again weigh accurately. Weigh the tube *B*, using *E* as a counterpoise. Introduce the boat in the decomposition tube *A*, remove the plugs from *B* and set them aside where they can be identified and attach *B* to *A*; finally, attach the aspirator to *B*.

**Decomposition of the Sample.** Open the pinch cock to the aspirator till a barely continuous stream of water flows, then begin to heat the muffle cautiously, starting at the end nearest the Marchand tube. Drops of water will soon begin to appear at the end of *A* but will gradually disappear as it becomes hotter. Gradually extend the heating to the middle of the muffle and increase the temperature till the bottom begins to show a barely perceptible redness when viewed from above. At the end of twenty

## 100 FUNDAMENTALS OF QUANTITATIVE ANALYSIS

minutes about 2 liters of air should have been drawn through the apparatus, the condensed water should have disappeared from *A*, and but little water should be left in the sample. If at any time the temperature is increased too rapidly, or the rate of flow from the aspirator is too slow, water vapor may accumulate back of the boat and some of it may be absorbed by *C*. If the accumulation is large it is usually shown by the appearance of drops between *C* and the boat. It is desirable, therefore, to keep this part of the tube cold in order to make this observation possible.

If the aspirator is now empty, remove the burner long enough to replace with a full one, again connect with *B*, and draw 2 liters of air through *A* as before. Finally, disconnect *B*, close its end, allow to stand twenty minutes, and weigh as before. Calculate the percentage of water present.

**Further Details Regarding the Process.** After the apparatus is once charged, the entire procedure can be completed in an hour. Duplicate determinations should agree to within one part in 200. The Marchand tube can be used safely for five determinations before recharging is necessary, but it is desirable to shake out the water which accumulates in the bulb-like enlargement after each determination.

### V. Questions and Problems. Series 7

- ✓ 1. A hydrate of  $\text{CdSO}_4$  is found to contain 18.71 per cent of water; what is its probable formula?  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$
- ✓ 2. A sample of a hydrated salt is found to contain 34.21 per cent of water; it is then found that the hygroscopic water present is 1.02 per cent. Calculate the percentage of water in the dry sample. *Ans.* 33.53.
- ✓ 3. Suggest procedures which might be applied to the liberated gas and the residual solid resulting from heating a hydrated sulfate, in order to ascertain the temperature at which the anhydrous salt begins to decompose at an appreciable rate.
- ✓ 4. A liter of dry air, measured at  $20^\circ \text{C}$ . and 760 mm., is passed through a vessel containing water kept at the same temperature. Assuming that the vapor pressure of water at  $20^\circ \text{C}$ . is 17.36 mm., that the air becomes saturated with water vapor and that the total pressure is 760 mm., what is the volume of the mixture? *Ans.* 1.033 liters.

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5. Twenty liters of dry air, measured at  $20^{\circ}\text{C}$ . and 760 mm., are slowly passed through a long tube, kept at  $50^{\circ}\text{C}$ . and charged with a certain hydrate, and then through an absorbing system. Assuming that the air attains equilibrium with the hydrate and that the absorbing system gains 0.391 gram in weight, what is the dissociation pressure of the hydrate? *Ans.* 19.35 mm.

6. The dissociation pressure of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  is 11.6 mm. at  $35^{\circ}\text{C}$ . Vessels containing  $\text{BaCl}_2$  and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  are placed in three different desiccators kept at  $35^{\circ}\text{C}$ . and containing (a) water, (b) 48 per cent sulfuric acid and (c) 60 per cent sulfuric acid. Assuming that the vapor pressure of water is 41.8 mm., that of 48 per cent sulfuric acid is 18.1 mm., and of 60 per cent sulfuric acid is 7.4 mm., what changes, if any, should take place in each case? What will determine whether these changes will be complete?

7. Calculate the percentage of  $\text{Na}_2\text{CO}_3$  in a mixture of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  and  $\text{NaCl}$  assuming that 2.0123 gm. of the mixture yielded 0.4013 gm. of water when heated under such conditions as to convert all the  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  into  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . *Ans.* 35.19.

## CHAPTER VIII

### DETERMINATION OF CARBON DIOXIDE IN LIMESTONE BY - THE EVOLUTION METHOD

#### I. Facts upon Which the Determination is Based

**Choice of Method.** The value of a sample of limestone for many purposes depends upon the percentage of carbon dioxide which it contains. The determination can be made by ascertaining the loss which takes place when a known weight is ignited in a crucible, but the method is inaccurate if the sample contains water, graphite, organic matter, ferrous compounds, or pyrite, all of which may be present in small amounts and cause changes in weight when ignited. If any one of these is known to be present, the carbon dioxide should be separated by the addition of an acid, as described on page 90, or in an alkalimeter. The use of the alkalimeter devised by Bunsen (Fig. 25) is described here.

**Choice of Reagent.** The most important components of limestone are carbonates of calcium and magnesium, but small quantities of ferrous carbonate and manganese carbonate are frequently found. All of these substances are but slightly soluble in water and therefore are not affected by solutions of organic acids or of mineral salts in which the concentration of hydrogen ion is below a certain minimum. Solutions of sulfuric acid give slow and incomplete decomposition owing to the formation of calcium sulfate, which forms an impervious coating on the particles of carbonates. Solutions of either hydrochloric or nitric acids give rapid and complete decomposition, but the use of the latter is not advisable owing to the ease with which the nitrate ion is reduced to nitric oxide and nitrogen dioxide by ferrous iron, pyrite, or organic matter. Hydrochloric acid therefore is commonly used; the amount and concentration of the solution used

must be adapted to the amount and character of the sample if loss of hydrogen chloride vapor is to be avoided. The concentration of hydrochloric acid needed to effect rapid and complete decomposition increases with the percentage of magnesium carbonate. Samples which contain much clay or other silicates, which are slowly acted upon by hydrochloric acid, are difficult to decompose owing to the gelatinous silica with which the sample becomes coated. A two-molal solution is sufficiently concentrated for the complete decomposition of most samples. Since the hydrogen chloride vapor in equilibrium with such a solution at 25° C. is about 0.001 mm., the error from this source at this temperature must be small. Although the vapor pressure increases rapidly with the temperature, it can be shown by a direct experiment that no hydrogen chloride can be detected in the air which has been passed through a bulb containing hydrochloric acid of this concentration even up to 80° C.

**Possible Sources of Error.** The errors involved in weighing a Bunsen apparatus are necessarily large owing to the weight and surface area. They should be reduced as much as possible by using a counterpoise as suggested on page 20. Further, it is desirable to reduce the percentage error from this source by weighing out a large amount of the sample. No difficulty is experienced in using as much as 2 grams in an apparatus of normal size in which the capacity of the acid reservoir is as much as 15 cc.

The carbon dioxide is necessarily saturated with water vapor, which must be removed before it is permitted to escape. Granular calcium chloride can be depended upon to remove all but negligible amounts of water from the escaping gas, provided it is not passed through the absorbing tube too rapidly. Since some samples of calcium chloride contain calcium oxide, and therefore absorb carbon dioxide, the drying tube should be saturated with the gas before use. Water saturated with carbon dioxide at atmospheric pressure and 20° C. contains 1.689 grams of carbon dioxide per liter, but the amount is reduced, in accordance with the law of Henry, by decreasing the pressure of carbon dioxide in the vapor phase. Since ordinary air contains only about 0.03 per cent of carbon dioxide, the actual solubility in water



saturated with air is very small. The rate at which supersaturated solutions lose their excess of dissolved carbon dioxide is low unless the solutions are heated in a current of air to  $60^{\circ}\text{C}$ . or more. The increased temperature and the presence of soluble salts, such as those resulting from the decomposition of the sample, reduce the solubility still further.

A further reason for substituting air for the carbon dioxide left in the apparatus after decomposition is that its weight is somewhat greater than the air present when the apparatus is weighed before decomposition of the sample.

## II. Preparation of the Apparatus

Clean the three parts, *A*, *B*, and *C*, of a Bunsen apparatus (Fig. 25), by rinsing with acid, if necessary, and with water, then allow to drain, and wipe the outer surfaces with a clean cloth. Dry the inner surface of tube *C* by heating either in an oven at  $100^{\circ}\text{C}$ . or cautiously over a wire gauze. Wipe dry also with a narrow strip of cloth the inner surface of the tubular portion of *A*.

Charge the drying tube by placing a small wad of cotton in its enlarged end, filling to within 1 cc. of the other end with lumps of dry granular calcium chloride of about the size of grains of wheat, covering with a second wad of cotton, and closing with a cork which is provided with an inlet tube of small diameter.

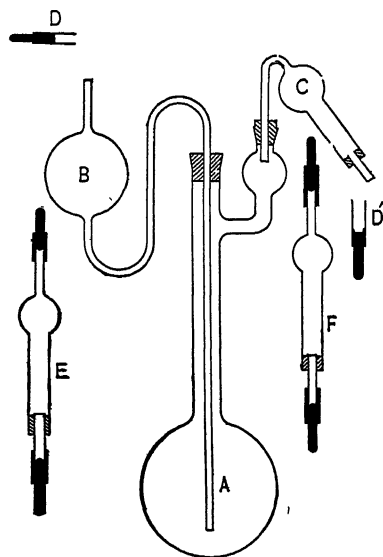


Fig. 25.—Bunsen's alkalimeter.

Press the cork into the tube till flush with its end and cover with a little sealing wax. Prepare in like manner an additional calcium chloride tube similar to *E*.

See that the corks used to connect *A* with *B* and *C* make tight joints. In order to test the matter put the apparatus together, close the open end of *C* with the finger and by gentle suction on the open end of *B* ascertain whether the apparatus is tight. Slight leaks are not usually of much significance as the pressure within the apparatus should never be large.

### III. Detailed Method of Procedure

**Charging the Apparatus.** Prepare a long narrow sample tube, which is small enough to pass into the flask *A*, by sealing up one end of a piece of thin-walled glass tubing and closing the other end with a cork, and charge with about 2 grams of sample. Weigh the tube accurately, and deliver its contents without loss into the bottom of flask *A* then withdraw the sample tube and again weigh accurately.

Pour about 15 cc. of 6 N hydrochloric acid into a small beaker, insert the shorter of the two tubes attached to the reservoir *B* into the acid, suck up about 10 cc. of the acid, then remove the tube *B* and invert so that the shorter tube again stands above the acid. Carefully remove the acid which adheres to the shorter tube by narrow shreds of filter paper. Next, unite *A*, *B*, and *C* as shown in the figure, place the plugs *D* and *D'* over the two open ends, let the apparatus stand, preferably supported in a large beaker, in or near the balance room for a half hour, and then weigh accurately, using a 200-cc. flask, which has also stood in the balance room for the previous half hour, as a counterpoise.

**Decomposing the Sample.** Remove the plugs *D* and *D'*, and set aside where they cannot be mixed with the plugs belonging to *E*. Next, cause the acid to siphon over, drop by drop, from *B* to *A*, controlling the rate of flow by holding the finger against the end of *B* and preventing any of the liberated gas from escaping through the reservoir tube. When all of the acid has been drawn into *A*, and when little or no carbon dioxide is being given off in the flask (this should require about fifteen minutes if the sample has been finely ground), heat the bulb *A* cautiously, avoiding a temperature in excess of 60° C. Next attach *E* to the free end of *B* and an aspirator to the free end of *C*, and draw about 1500 cc.

of air through the aspirator, still keeping the bulb of *A* warmed. This should take about twenty minutes. Disconnect *E* and the aspirator, and replace by the plugs *D* and *D'*. Allow the apparatus to stand and then weigh it, as before. Calculate the percentage of carbon dioxide formed.

**Further Details.** Before discarding the residue left in the decomposition bulb, add to it a few cubic centimeters of 6 N hydrochloric acid and note whether any more carbon dioxide is liberated. If gas is evolved, either the sample used was too large for the amount of acid added or it was one which required an unusually large concentration of acid for decomposition. With some samples it may be necessary to use acid whose strength is so great that the residual solution may give appreciable loss of hydrogen chloride vapor at 60° C. The insoluble residue usually consists of quartz and insoluble silicates, especially kaolin and other clay-like minerals, and graphite. Most samples of pyrite are not acted upon appreciably by 2 N acid.

The entire analysis, exclusive of the two half-hour periods before weighing, can be completed in an hour. Duplicate determinations should agree to within one part in 200.

#### IV. Questions and Problems. Series 8

1. Calculate the molal concentration of hydrochloric acid in the residual solution of a determination of carbon dioxide in a sample composed of 90 per cent calcium carbonate, 5 per cent of magnesium carbonate, and 5 per cent of silicon dioxide, assuming that 2 grams of sample and 10 cc. of 6 N acid were used.

*Ans.* 2.17.

2. Assuming that the partial pressure of water vapor in the gas which escapes during the decomposition of 2 grams of a sample of pure calcium carbonate and in the 1500 cc. of air drawn through the apparatus after decomposition, is 1 mm., what percentage error and what departure would be caused by loss of water, assuming that the percentage of carbon dioxide is reported?

*Ans.* 0.22 and 0.10.

3. What assumption is made in the preceding problem which greatly increases the calculated error due to loss of water vapor above that which the actual conditions of the determination demand?

4. It is found that a sample composed of calcium and magnesium carbonates and 8 per cent of silicon dioxide contains 43.3 per cent of carbon dioxide. What percentages of the two carbonates are present? (See page 46 for methods of solution.)

*Ans.* 57.44 and 34.56.

5. Assuming that the capacity of the Bunsen apparatus is 60 cc. calculate the volume of air which should be passed into it to reduce the carbon dioxide left after the decomposition to 1 mg., assuming first, that all the air used was uniformly mixed with the carbon dioxide present, and second, that none of it was so mixed.

*Ans.* 6570 cc. and 59.46 cc.

6. Discuss the factor affecting the completeness of the reactions between (a) ferrous sulfate, potassium nitrate, and sulfuric acid, assuming that ferric ion and nitric oxide are formed; (b) manganese dioxide, oxalic acid, and sulfuric acid, assuming that manganous ion and carbon dioxide are formed; (c) calcium carbide and water, assuming that acetylene is formed. Describe all the determinations which might be based upon these reactions.

7. How would the result for the determination of  $\text{CO}_2$  in limestone be affected if the sample contained small amounts of (a) pyrite, (b) manganese dioxide, (c) calcium phosphate, (d) gypsum, (e) sodium sulfate?

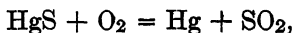
8. A sample of baking powder, which consists of equivalent proportions of sodium bicarbonate and potassium bitartrate ( $\text{C}_4\text{H}_5\text{KO}_6$ ), mixed with starch, yields twelve per cent of  $\text{CO}_2$  when treated with water in a Bunsen apparatus; calculate the percentage composition of the baking powder.

## CHAPTER IX

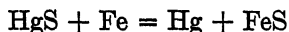
### DETERMINATION OF MERCURY IN AN ORE

#### I. Facts upon Which the Determination is Based

**Thermal Decomposition of Mercury Compounds.** The compounds of mercury are characterized by the ease with which they decompose when heated to moderately high temperatures. This peculiarity is dependent upon two properties of the element; first, its volatility, and second, its weakly basic properties as shown by the position it occupies in the electrode potential series. Most of its solid compounds are completely decomposed when heated to 500° C. either with or without the admixture of some basic reagent, such as calcium oxide or sodium carbonate. The ores of mercury which are of commercial importance contain either metallic mercury, or mercuric sulfide in the form of minerals known as cinnabar or metacinnabarite. When mercuric sulfide is heated in air, it begins to react with oxygen according to the equation,



and even between 300° and 450° C., the reaction is both rapid and complete. If the sulfide is mixed with some iron filings, the reaction



is complete and rapid even at somewhat lower temperatures. When heated with calcium oxide, the reaction



takes place although it is probable that small amounts of calcium sulfate and other sulfur-containing compounds are also formed. This reaction is also rapid and complete at 450° C. Since the

vapor pressure of mercuric sulfide at 400° C. is 25 mm., it is probable that in all of these processes the actual decomposition results from the action of the vapor of mercuric sulfide or the solid reagents. It is easily possible therefore to separate the mercury which is present in an ore, either as the metal or as the sulfide, by mixing the finely powdered ore with one or both the reagents named and heating to 450° C.

**Condensation of Mercury Vapor.** The vapor pressure of mercury vapor varies rapidly with changes in the temperature. At 20° C. it is 0.0013 mm., at 100° C. it is 0.28 mm., at 200° C. it is 17.5 mm., and at 357.3° C. it is 760 mm. If, therefore, a gaseous mixture containing mercury vapor is cooled, even at 100° C., the percentage of mercury left in the vapor is small, and if the concentration of mercury vapor in the original mixture is not too small the fraction left uncondensed is small. For example, if 50 cc. of air is associated with 0.05 gram of mercury, both at 450° C., the mixture should occupy a volume of 64.81 cc. if the total pressure is 760 mm. When the mixture is cooled to 100° C. nearly all the mercury is condensed and the volume of air is reduced to 25.8 cc. The volume of mercury vapor associated with this volume of air, assuming its partial pressure is 0.28 mm. must be

$$25.8 \times \frac{0.28}{760 - 0.28} = 0.0095 \text{ cc.}$$

and its weight must be 0.00006 gram. Hence the percentage of mercury left uncondensed must be,

$$\frac{0.00006}{0.05} \times 100 = 0.12.$$

If the volume of air associated with the 0.05 gram of mercury had been 100 cc., the percentage of mercury left uncondensed would have been 0.24. It is evident therefore that the volume of air or other gases associated with the liberated mercury vapor should be kept as small as possible if the loss due to incomplete condensation is to be kept small.

If the decomposition of the ore is made to take place in a closed vessel, the pressure, due to the air present, increases owing to

the increased temperature, and the pressure due to mercury vapor also increases from zero to a value which depends upon the temperature, volume, and amount of mercury. In order to discuss the matter specifically we will assume that ore sufficient to yield 0.05 gram of mercury is decomposed in a closed retort and that the volume of air it contains, at 760 mm. and 20° C., is 22 cc. If the retort is heated to 450° C. the pressure due to air must be 1875 mm. and that due to the mercury vapor becomes 511 mm. If now the mixture is cooled to 100° C. practically all the mercury vapor is condensed because the pressure of the saturated vapor at this temperature is only 0.28 mm. The actual amount of mercury vapor associated with the 22 cc. of air can be calculated to be 0.00005 gram or one-tenth of 1 per cent of the original 0.05 gram.

In order to collect and weigh the condensed mercury vapor, advantage may be taken of the tenacity with which liquid mercury attaches itself to plates of gold, silver, and copper. When mercury condenses on such plates it forms a thin film or series of very fine droplets and, although they can be dislodged by brushing or, if the film is thick, by vigorous shaking, no difficulty is experienced in accurately determining the weight of mercury adhering to such plates. After weighing, the mercury can be expelled by heating to about 400° C., and such plates can be used for many determinations. If plates of gold or silver are used, their weights remain practically constant; if a plate of copper is used, its weight increases slightly owing to oxidation.

**Apparatus for the Determination.** Many different forms of apparatus, designed to make use of the procedure outlined above, have been devised. The apparatus designed by Whitton,<sup>1</sup> which is represented in Fig. 26, is the most convenient. It consists of an iron crucible *A*, of about 24-cc. capacity; a sheet of silver foil *C*, about 45 mm. square and 0.2 mm. thick; a brass dish *B*, which is kept full of water; an iron shield, which protects the foil from the flame used to heat the crucible; and a clamp *D*, by means of which the crucible, foil, and dish are held together and escape of the vapor from the crucible permitted.

<sup>1</sup> See Mineral Industry, 17, 751 (1908).

It is found that a piece of foil of the size named does not readily retain more than 0.07 gram of mercury without danger of appreciable loss, and the amount of sample used for a determination should yield from 0.04 to 0.07 gram. The method is especially adapted for the determination of mercury in commercial ores, that is ores in which the percentage of mercury rarely exceeds five, and is, usually very much less.

The preceding calculations relating to the condensation of mercury vapor correspond roughly to the conditions represented if the determination is made in the apparatus described. They assume that iron filings only are used for the reagent and therefore an additional increase in pressure due to the formation of oxygen gas is eliminated. The iron filings have the further advantage of being a better conductor of heat than calcium oxide and making it possible to bring the entire mixture to the desired temperature more rapidly than if calcium oxide were used.

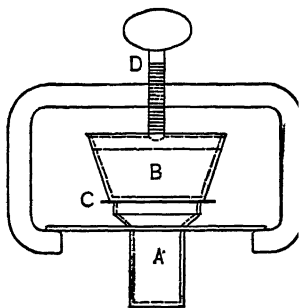


Fig. 26.—Whitton's apparatus for determination of mercury.

The assumption is made that no vapors escape from the retort, but experience shows that this is not essential to the obtaining of accurate results. The method also assumes that the mercury condenses on the silver plate only, which assumption is justifiable if the plate is kept at a much lower temperature than the crucible during the earlier part of the cooling process. The formation of sulfur dioxide from the oxygen of the air has been disregarded, but, since this involves no volume change, it has no effect upon the total pressure.

**Sources of Error.** Errors may result from the condensation of certain substances on the silver foil with the mercury. Small amounts of water may condense, but this is avoided by drying the ore and reagents before use. Organic matter, derived from the iron filings or the ore, may also deposit on the foil. If all grease, with which the filings are sometimes contaminated, is removed by washing with gasoline before using, and if filings derived from



low-carbon alloys are used, the deposition of organic matter from this source can be eliminated. If the ore contains bituminous or other forms of organic matter, which is not unusual, a small amount of potassium chlorate should be added to the mixture used for decomposition of the ore, but in such a case calcium oxide rather than iron filings should be used for the decomposition. Mercuric sulfide may volatilize as such and condense on the silver foil, but this is not likely to happen if the vapors formed when the mixture is heated are made to pass through a thin layer of iron filings. Sulfur, derived from iron pyrite, which is frequently associated with such ores, may also condense on the plate, but the addition of an excess of cupric oxide to the resulting mixture will prevent this.

The accuracy of the process depends ultimately upon the details of procedure used in heating the mixture of ore and reagents. Too high a temperature results in slight losses of mercury vapor; insufficient heating or too low a temperature results in incomplete decomposition. The proper conditions for the determination must be ascertained by actual experience with mixtures of known composition.

## II. Details of Procedure

**Charging the Apparatus.** It will be assumed that the sample used contains not more than 6 per cent of mercury, has been crushed fine enough to pass through an eighty-mesh sieve, and that neither organic matter nor pyrite is present in appreciable amounts.

Heat the silver foil until it shows a faint tinge of redness but avoid attaining its melting temperature of  $960^{\circ}\text{C.}$ , and then place it on a clean dry watch glass in a desiccator and set aside to cool. Weigh out about 3 grams of the properly prepared iron filings into the iron crucible, then about 0.7 gram of the ore, weighed accurately, and mix the two thoroughly by stirring with a glass rod. Tap the mixture until the surface is level and the charge well settled, and then cover with an additional gram of iron filings. Weigh the silver foil accurately to 0.1 mg. Place the crucible in the opening of the iron shield and support the latter on a ring stand. Place the silver foil on the crucible and adjust the

brass dish on the foil so that it is supported at all points by the crucible and the latter is completely covered by the foil and dish. Finally fasten the dish, foil, and crucible together firmly by means of the iron clamp.

**Decomposition of the Sample.** Fill the brass dish with water and heat the crucible with the flame of a burner which extends two-thirds of the distance between the bottom of the crucible and the shield and causes the water to boil vigorously within six minutes. Maintain it at this temperature fifteen minutes longer, replacing the evaporated water from time to time. Remove the burner, fill the dish with cold water, allow the crucible to cool for fifteen minutes, remove the foil, keeping the mercury-coated side uppermost, and weigh accurately. Calculate the percentage of mercury present. Expel the mercury from the silver plate by holding it, mercury-coated side uppermost, in the flame of a burner until fumes are no longer given off. Avoid inhaling the escaping fumes, which are poisonous. Next, stir the contents of the retort with a glass rod and again heat with the accurately weighed foil and cooling dish properly connected, in order to ascertain whether the first heating resulted in complete decomposition of the ore. If appreciable amounts of mercury are found by the second heating, it indicates that proper conditions for heating were not attained.

If the total weight of mercury found is much less than 0.05 gram a proportionally larger amount of sample should be used for a second determination, but the amount of reagent used for the determination need not be increased.

**Further Details Regarding the Method.** The simple procedure here described is entirely satisfactory for ores of the assumed composition. It is less satisfactory if large amounts of organic matter or sulfur are present owing to the additional reagents which must then be used. Such ores are best decomposed in tubes of pyrex glass, the liberated mercury allowed to condense on the sides of the tube, dissolved in nitric acid and determined in the resulting solution by means of a volumetric process. The details of this process have been worked out by Bouton and Duschak.<sup>1</sup>

<sup>1</sup> Technical Paper 277, Bureau of Mines. (1920.)

## Questions and Problems. Series 9

1. If a loosely covered crucible, which contains 22 cc. of air at  $20^{\circ}\text{C}$ ., is heated to  $450^{\circ}\text{C}$ ., and the expelled air cooled to  $100^{\circ}\text{C}$ . before it escapes, what volume is expelled? *Ans.* 16.66 cc.

2. What weight of mercury vapor is present in 1 liter of air which has been saturated with mercury vapor, assuming that the temperature is  $100^{\circ}\text{C}$ ., the total pressure is 760 mm., and the partial pressure of mercury vapor is 0.28 mm.

*Ans.* 0.0024 gram.

3. Calculate the pressure in a crucible which contains enough ore to yield 0.05 gram of mercury, and has a volume of 22 cc., if closed at  $20^{\circ}\text{C}$ . and 760 mm. and then heated to  $450^{\circ}\text{C}$ .

*Ans.* 2386 mm.

4. A flask which contains 0.1 gram of pure mercuric sulfide and 900 cc. of air, measured at  $20^{\circ}\text{C}$ ., is sealed and heated until the mercuric sulfide is completely changed into mercury vapor and sulfur dioxide. The gaseous mixture is then cooled to  $100^{\circ}\text{C}$ . What percentage of the mercury originally present as sulfide should be condensed?

*Ans.* 97.43.

5. Derive the simplified expression representing the application of the mass law to the three reactions given in the paragraph entitled "Thermal Decomposition of Mercury Compounds."

6. Would you expect the accuracy of the process here outlined to be greatly affected if the ore contained  $\text{MgCO}_3$  or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{As}_2\text{S}_3$  or  $\text{PbS}$ ?

7. Why should the decomposition of the ore be affected by use of calcium oxide rather than of iron filings if potassium chlorate is used to destroy organic matter? Give the reaction concerned.

## SECTION III

### PRECIPITATION PROCESSES

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#### CHAPTER X

#### GENERAL THEORY OF PRECIPITATION PROCESSES

**Equilibrium in Reactions Involving Precipitation.** All precipitation processes involve the formation of a new solid phase from a liquid phase and therefore involve heterogeneous equilibrium. The new solid phase may result from the addition of a liquid reagent such as alcohol, which reduces the solubility of the constituent which precipitates, or from a chemical reaction brought about by the addition of a reagent, or from the action of the electric current. Since the concentration of the substance precipitated, in the solution from which it separates, cannot exceed that of a saturated solution of that precipitate, the completeness of those reactions which result in the formation of precipitates is determined by the solubility of the precipitate. In all precipitation processes the mathematical expression which determines the completeness of the precipitation, and therefore the accuracy of the process, is simply

$$K = C,$$

where  $C$  is the concentration of the separated substance in the saturated solution from which it separates.

Most of the precipitates which find extended use in quantitative analysis are strong electrolytes and therefore are largely dissociated. If, in addition to being a strong electrolyte, the precipitate yields simple ions only, and if these ions are also strong, that is, are not appreciably hydrolyzed, the composition of the saturated solution is easily expressed. A saturated solution of silver chloride, for example, should contain concentrations of silver ion and chloride ion which equal the total concentration of dissolved silver

chloride. A saturated solution of magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ ), on the other hand, should yield only about 3 per cent of the  $\text{NH}_4^+$  and  $\text{PO}_4^{---}$  to which the molal solubility corresponds, owing to hydrolysis of both phosphate ion and ammonium ion. Certain precipitates also yield large proportions of complex ions. Thus silver cyanide forms  $\text{Ag}_2\text{CN}^+$  and mercurous chloride forms  $\text{Hg}_2\text{Cl}^-$ . All of these effects increase the apparent solubility of the precipitate which then becomes the sum of the concentrations of the original and derived ions.

**Methods of Determining Solubility.** The accurate determination of the solubility of the precipitates which are of importance in quantitative analysis presents many difficulties. The direct method is to prepare a saturated solution of the precipitate concerned, evaporate a known volume of it in a vessel of known weight and determine the increase in weight due to the dissolved precipitate. Since the solubility of such substances rarely exceeds a few milligrams per liter, the volume of solution evaporated must be large, and even under favorable conditions the percentage error of this method is large. It is by far the most reliable method of determining solubility since it shows the total concentration of all the substances present in the saturated solution.

Indirect methods, which depend upon measurement of the conductance of the saturated solution and comparison with that of solutions containing known concentrations of the same or similar compounds, have been more generally used.<sup>1</sup> Although such measurements can be made with a high degree of accuracy the results obtained are in many cases subject to a rather large degree of uncertainty, because the calculations used involve assumptions regarding the actual composition of the saturated solution and conductance of the ions present which are questionable. Another indirect method<sup>2</sup> involves determination of the concentration of some one of the ions present by measuring the electromotive force of a galvanic cell of which the solution is a component, as described in Chapter XIII. This method also yields good results provided the relation between the total concentration of the dissolved salt and that of the ion measured is accurately known.

<sup>1</sup> Kohlrausch, *Zeit. phys. Chem.* 64, 158 (1908).

<sup>2</sup> Goodwin, *Zeit. phys. Chem.*, 13, 645 (1894).

**Supersaturated Solutions.** Although the solubility of any pure substance has a constant value provided the temperature is constant and the particles of which it is composed are of uniform size, the rate at which the equilibrium condition is attained is often slow. It frequently requires vigorous stirring for hours, or even days, to completely saturate a solution with a given solid. On the other hand it is easily possible to prepare solutions containing much larger concentrations of the soluble substance than the solubility constant demands. Such solutions are designated as "supersaturated." They usually result when a solvent is saturated with a solute at a given temperature, and the temperature is then changed to one at which the solubility is less; or when the solid is formed in the solution as the result of changes in the composition of the solvent, or the addition of a reagent which precipitates the solid. The excess of dissolved substance may usually be made to separate by agitation, but even when agitated vigorously the process is often a slow one. The only guarantee that a solubility value has been correctly ascertained is that closely agreeing results were found when equilibrium was attained in solutions which were both super-saturated and under-saturated.

**Solubility and Size of Particles.** Equilibrium in a saturated solution represents a state of balance between the processes of solution and that of precipitation. This takes place only at the surface of contact between the solid and liquid phases and the equilibrium should therefore be effected to some extent by the surface exposed as compared with the total amount of solid concerned. The total amount of surface exposed by a given weight of precipitate increases with the number of particles into which the precipitate is divided. The actual increase of surface area depends upon the form of the individual particles. The surface area of 1 gram of barium sulfate when in the form of a single sphere is 1.83 sq. cm.; if in the form of 1000 spheres of equal size the area is 18.3 sq. cm. It is not surprising therefore to find that the solubility of a precipitate increases somewhat as the size of the particles of which it is composed decreases. In a series of experiments on the solubility of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) it was shown<sup>1</sup> that solutions which had been thoroughly saturated through long

<sup>1</sup> Hulett, *Zeit. phys. Chem.*, 37, 385 (1901).

contact with particles of moderate size showed a decided increase in concentration as soon as a small amount of more finely divided particles was added. On long standing these very fine particles all disappeared and the solubility constant attained its original value. Solutions saturated with particles whose average diameter was 0.002 mm. were found to contain 2.085 grams of calcium sulfate per liter; if saturated with particles whose average diameter was 0.0003 mm., the concentration increased to 2.476 grams per liter; that is, decreasing the size of the particles from 0.002 to 0.0003 mm. increased the solubility by about 19 per cent. Further experiments showed that the solubility remained practically constant if the average diameter of the particles equalled or exceeded 0.002 mm., and this value was designated the "normal solubility." Experiments with barium sulfate gave even more striking results. When precipitated from a boiling solution, the particles showed an average diameter of 0.0018 mm. and gave a normal solubility of 0.0023 gm. per liter; when the size was reduced to correspond to an average diameter of 0.0001 mm., the solubility increased to 0.00415 gram and the naturally occurring salt reduced to a still finer state of division gave 0.00618 gram.

It seems probable that there is a tendency for all finely divided substances, in contact with their saturated solutions, to increase the size of the individual particles up to a certain maximum, and for the saturated solution to attain a certain normal solubility. If this is true, solutions saturated with a solid, some of the particles of which are below the normal size, are supersaturated with respect to the particles which exceed the normal size, and on standing some of the dissolved substance should be deposited upon the larger particles; further, since the solution would then be under-saturated with respect to those particles which are smaller than the normal size, these would pass into solution. The total effect should be the disappearance of all particles whose size is below normal. This explains why it is sometimes possible to change the character of a precipitate, which is too fine to be retained by a filter to such an extent as to make filtration possible, by digesting it with its saturated solution.

**Effect of Temperature and Pressure on Solubility.** The effect of temperature upon the solubility of precipitates depends upon

the amount of heat absorbed or liberated when such precipitates are dissolved in nearly saturated solutions. If heat is absorbed, as is usually the case, increasing the temperature increases the solubility; if heat is liberated, increasing the temperature decreases the solubility. Since but few determinations of this kind have been made, it is not usually possible to calculate the effect of changes of temperature upon solubility, and most of the direct determinations of solubility have been made at a standard temperature only. The change in the solubility of silver chloride and of barium sulfate, expressed in milligrams per liter, was determined to be as follows:<sup>1</sup>

	At 18°	At 25°	At 50°	At 100°
Silver chloride.....	1.50	.....	5.21	21.02
Barium sulfate.....	2.20	2.46	3.35	3.89

These figures show that the error of a quantitative process may be appreciably increased by increasing the temperature at which the precipitate is made.

A further possible effect of varying the temperature is to change the hydration, that is, the number of molecules of water associated with one molecule of the precipitate concerned, and therefore its solubility. Thus, magnesium ammonium phosphate separates from the saturated solution as a monohydrate if the temperature exceeds 48°, and as a hexahydrate at lower temperatures. Since the former is more soluble it is preferable to avoid its formation. The "transition temperature," that is, the temperature at which both hydrates are in equilibrium with the saturated solution depends upon the vapor pressure of the solution, and therefore upon the concentrations of all the substances present in it.

The usual effect of increasing pressure is to increase solubility, but the change is insignificant unless the increase amounts to many atmospheres.

**Variation in the Composition of Precipitates.** The obvious requirement that all precipitates used for quantitative determination should represent a compound of known composition, or should be readily convertible into such, eliminates the possibility of using a large number of precipitates which might be suggested

<sup>1</sup> Melcher, Jour. Am. Chem. Soc., 32, 55, (1910).



in this connection. Some of the precipitates used in qualitative analysis are found to be mixtures, the proportions of which vary with very slight variations in the conditions of precipitation. This applies especially to salts of weak acids, such as borates, phosphates, arsenates, carbonates, and ferrocyanides, which are partially hydrolyzed, and may form basic salts, containing hydroxyl in addition to the anions named; or to complex salts, which contain more than one of the anions named; or to double salts, which contain more than one cation. Such compounds may be less soluble than the salt of normal composition, or, owing to differences in the rate at which they are formed, may separate in small amount with the normal salt and form a permanent component of the mixture even though equilibrium conditions would require that they be transformed into the normal salt. The composition and relative proportions of the solid components of such mixtures often depend upon what seems to be unimportant and insignificant details of procedure, which are difficult to control accurately. It is easily shown that the precipitate formed when solutions of lead acetate and sodium chromate are mixed vary greatly in color, and it can be shown by carefully controlled experiments that the precipitate varies considerably from the composition of normal lead chromate. In some cases it is possible, by careful control of the conditions of precipitation, to insure precipitates of constant composition even in these cases of variable composition. Thus magnesium, zinc, and manganese can be separated as double phosphates of ammonium of practically constant composition under certain definite conditions, but this is not true of calcium and most of the insoluble phosphates.

Similar difficulties arise in determining certain metals of variable valences by precipitating them as hydrated oxides and igniting. It seems to be certain that the oxide obtained by igniting the precipitate known as ferric hydroxide is not pure ferric oxide, and that obtained by igniting the hydrated dioxide of manganese is not pure  $Mn_3O_4$ . Although both procedures are used as quantitative processes these methods should be avoided for the determination of these elements if a high degree of accuracy is demanded.

**Table of Solubilities.** In column four of Table II are given the solubilities, expressed in milligrams per liter, of some of the pre-

precipitates which are of especial importance in quantitative analysis. Those marked *D* were obtained by a direct method, that is, either by evaporating a definite volume of the saturated solution or by determining its concentration by a chemical process. The others were obtained by indirect methods, and the uncertainties involved in the assumptions upon which the calculations used were based are in some cases large. Additional uncertainties due to possible variations in the composition of the solid used, the nature of the ions present, and the degree of hydrolysis, are indicated in column two. For the very slightly soluble precipitates the figures given probably represent only the order of magnitude of the true value. They may be used, however, as a starting point for the discussion of the probable error of precipitation processes. In most cases only two significant figures are given, and not more than two significant figures need be retained in calculations in which these values are used. The data in this table have been compiled and in some cases recalculated from the results of the work of many investigators. Some of the more comprehensive papers which discuss in detail the theory of the methods used in determining solubilities and solubility products are listed.<sup>1</sup>

**/Effect of Additional Substances on the Solubility of Weak Electrolytes.** A saturated solution of a weak electrolyte, such as benzoic acid, contains in addition to benzoic acid, hydrogen ion and benzoate ion. If we represent the total number of moles (ionized and unionized) in 1 liter of such a solution by *m*, and the fraction dissociated by *x*, then *mx* must represent both ( $\text{H}^+$ ) and ( $\text{C}_6\text{H}_5\text{COO}^-$ ), and *m*(1 - *x*) must represent the undissociated  $\text{C}_6\text{H}_5\text{COOH}$ . Assuming further that dissociation is a process which obeys the mass-law, the relation:

$$(mx) \cdot (mx)K = m(1 - x)$$

<sup>1</sup> Kohlrausch and Rose, *Zeit. physik. Chem.*, 12, 24 (1893); Bodländer, *Zeit. physik. Chem.*, 35, 31 (1900); Goodwin, *Zeit. physik. Chem.*, 13, 645 (1894); Bodländer and Storbeck, *Zeit. physik. Chem.*, 31, 465 (1907); Noyes and Kohl, *Zeit. physik. Chem.*, 42, 342 (1903); Sherrill, *Zeit. physik. Chem.*, 43, 732 (1903); Hill, *Jour. Am. Chem. Soc.*, 31, 74 (1908); Kohlrausch, *Zeit. physik. Chem.*, 64, 158 (1908); Melcher, *Jour. Am. Chem. Soc.*, 32, 54 (1910); McCoy and Smith, *Jour. Am. Chem. Soc.*, 33, 473 (1911); Beebe, *Zeit. Anal. Chem.*, 49, 557 (1910).

TABLE II  
SOLUBILITIES OF PRECIPITATES

Name of Precipitate	Remarks	Temperature	Solubility in Mg	Solubility Product
Antimony trisulfide	Assumed to be completely hydrolyzed	18°	1.75	
Arsenic trisulfide	Assumed to be completely hydrolyzed	18°	0.52	
Barium carbonate	Carbonate assumed to be half hydrolyzed	25°	35.4	$8.1 \times 10^{-9}$
Barium sulfate	Dissociation assumed complete	18°	2.3	$1.1 \times 10^{-10}$
Bismuth trisulfide	Assumed to be completely hydrolyzed	18°	0.18	
Cadmium sulfide	Assumed to be completely hydrolyzed	18°	1.30	
Calcium carbonate	Calculated to be two-thirds hydrolyzed	25°	16.6 D	$2.75 \times 10^{-8}$
Calcium oxalate	Solid $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	25°	6.7 D	$2.6 \times 10^{-9}$
Calcium sulfate	Solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in solution, about 52 per cent dissociated	18°	2020 D	
Cobalt sulfide	Assumed to be completely hydrolyzed	18°	0.38	
Cupric sulfide	Assumed to be completely hydrolyzed	18°	0.34	
Cuprous iodide	Assumed to be completely dissociated	18-20°	0.42	$5.0 \times 10^{-12}$
Cuprous sulfide	Assumed to be completely hydrolyzed	16-18°		$2.2 \times 10^{-47}$
Cuprous sulfocyanate		18°		$1.6 \times 10^{-11}$
Ferric hydroxide	Solid $\text{Fe}(\text{OH})_3 \cdot \text{XH}_2\text{O}$	18°	$4.8 \times 10^{-5}$	$1.1 \times 10^{-36}$
Lead Carbonate	Probably largely hydrolyzed	18°	2.14	$3.3 \times 10^{-14}$

Lead chromate	Calculated to be 57 per cent hydrolyzed	18°	0.10	$1.8 \times 10^{-14}$
Lead oxalate	Dissociation assumed to be complete	18°	1.6	$2.9 \times 10^{-11}$
Lead sulfate	Assumed to be 30 per cent hydrolyzed	18°	39.4	$6.1 \times 10^{-9}$
Lead sulfide	Assumed to be completely hydrolyzed	18°	0.86	
Magnesium ammonium phosphate	Solvent $1 \cdot \text{IN}(\text{NH}_4)\text{OH}$	20°	98.	
Magnesium carbonate	Calculated to be 38 per cent hydrolyzed	12°	543	$2.6 \times 10^{-6}$
Magnesium hydroxide	Solid $\text{Mg}(\text{HO})_2 \cdot x\text{H}_2\text{O}$	18°	11.8	$3.4 \times 10^{-11}$
Manganese hydroxide	Solid $\text{Mn}(\text{HO})_2 \cdot x\text{H}_2\text{O}$	18°	1.9	$4.0 \times 10^{-14}$
Mercuric sulfide	Assumed to be completely hydrolyzed	25°	0.012	
Mercurous chloride	Solid $\text{Hg}_2\text{Cl}_2$ ; solution contains $\text{Hg}_2^{++}$ , $\text{Cl}^-$ and $\text{HgCl}_2^-$	25°	0.45	$3.5 \times 10^{-18}$
Silver arsenate	Probably largely hydrolyzed	20°	8.5	
Silver bromide	Dissociation assumed complete	25°	0.124	$4.3 \times 10^{-13}$
Silver chloride	Dissociation assumed complete	18°	1.5	$1.1 \times 10^{-10}$
Silver chromate	Dissociation assumed complete	18°	25.6	$1.7 \times 10^{-12}$
Silver iodide	Dissociation assumed complete	25°	0.002	$1.0 \times 10^{-16}$
Silver iodate	Dissociation assumed complete	25°	53.4	$3.6 \times 10^{-8}$
Silver oxide	Composition of solid questionable	25°	27.0	$4.6 \times 10^{-8}$
Silver sulfide	Assumed to be completely hydrolyzed	18°	0.014	
Silver sulfocyanate	Dissociation assumed complete	25°	0.18	$1.2 \times 10^{-12}$
Strontium carbonate	Assumed to be 60 per cent hydrolyzed	25°	14.7	$1.6 \times 10^{-9}$
Strontium sulfate		17°	.097	
Strontium oxalate	Solid $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	18°	46.0	$6.7 \times 10^{-8}$
Zinc sulfide	Assumed to be completely hydrolyzed	18°	6.8	

must be true. If we assume that  $m(1 - x)$ , that is, the solubility of unionized benzoic acid, has a constant value, since  $K$  is also a constant the product  $(mx)(mx)$  must also be a constant for all solutions of  $H^+$  and  $C_6H_5COO^-$ , which are saturated as to benzoic acid. Further, this should be true for all electrolytes for which such assumptions are justifiable. This product was first designated "solubility product" by Ostwald and has been widely used in discussing the solubility of electrolytes. So long as we are concerned with water and benzoic acid only, the total solubility must have a constant value, but it can be shown that this value should vary if we are concerned with solutions containing additional electrolytes which yield either  $H^+$  or  $C_6H_5COO^-$ . This is a necessary consequence of the fact that the addition of such substances as nitric acid, which increases  $(H^+)$ , or of sodium benzoate, which increases  $(C_6H_5COO^-)$ , must make the product of  $(H^+)$  and  $(C_6H_5COO^-)$  greater than it was in the original saturated solution, but if we still assume that this has a fixed value some kind of readjustment must take place if true equilibrium is to be maintained. The simplest readjustment would be the formation of additional amounts of unionized acid, and the separation of the same amount in solid form. It is evident that the solubility of benzoic acid in water should be decreased by the addition of any electrolyte which increases either  $H^+$  or  $C_6H_5COO^-$ , and that any strong acid or any salt of benzoic acid should be especially effective in reducing the solubility. However, since benzoic acid is a weak electrolyte, that fraction of its solubility due to its dissociated form is relatively small and therefore the total change in solubility, even if  $(H^+)$  or  $(C_6H_5COO^-)$  could be reduced to zero, would be small. Assuming that the degree of dissociation of benzoic acid in a saturated solution is accurately determined by conductance measurements, it should be possible to calculate the actual value of the solubility product, and from it the decrease in the solubility resulting from the addition of known amounts of an electrolyte whose dissociation is known.

**Effect of Additional Substances on the Solubility of Strong Electrolytes.** Application of the solubility product principle to saturated solutions of strong electrolytes involves a number of

difficulties. Such electrolytes do not dissociate in accordance with the requirements of the mass-law, that is, when the ionic concentrations to which they give rise are determined by conductance methods. As noted on page 66 the effective concentrations of the ions depend upon an additional factor known as the activity coefficient, which cannot be calculated from existing data except for a limited number of simple cases. If the precipitate is only slightly soluble, and if it yields only univalent ions, the activity coefficients, at least in most cases, do not greatly differ from unity. In dealing with such electrolytes, therefore, no very large error will arise if the distinction between activity products and solubility products be disregarded. The error involved in this procedure increases rapidly with increasing solubility of the precipitate, with the formation of di- or tri- rather than univalent ions, and with the presence of large concentrations of any other electrolytes. The method of using the solubility product principle under ideal conditions will therefore be illustrated by a specific example.

**Calculations by Means of Solubility Product Principle.** The solubility of silver chloride in pure water is 0.0015 gram or  $1.05 \times 10^{-5}$  moles per liter. This number must represent the concentration of both silver and chloride ion in the solution, and therefore  $(1.05 \times 10^{-5})^2$  or  $1.1 \times 10^{-10}$  must represent the solubility product. Quantitative determinations based upon the separation of silver chloride necessarily involve the presence of an excess of the precipitating agent used, and the error from solubility depends upon the solubility of silver chloride in solutions containing an excess of either soluble chloride or soluble silver salt, that is, in solutions in which the ratio of silver ion to chloride ion is greater or less than one. Let us assume that we precipitate the chloride ion in 200 cc. of a 0.2 molal solution of sodium chloride by the addition of silver nitrate in solid form, which will avoid appreciable changes in the volume. If first we add exactly 0.04 mole of silver nitrate the ratio of silver to chloride ion in the resulting mixture is one to one. Assuming that pure silver chloride is precipitated, the resulting solution must contain equal concentrations of silver and chloride ion, namely  $1.05 \times 10^{-5}$ . If next we add 0.0002 mole of silver nitrate practically all of it will remain

in solution, and since the volume is 200 cc. the concentration of silver ion will now attain a value slightly in excess of 0.001. Since, however,  $(\text{Ag}^+) \times (\text{Cl}^-)$  must always equal  $1.1 \times 10^{-10}$  chloride ion must be driven out of solution as insoluble silver chloride until the concentration is reduced to  $1.10 \times 10^{-10} \div 1 \times 10^{-3}$  or  $1.10 \times 10^{-7}$ . A more exact calculation would involve the solution of a quadratic equation. If  $x$  be used to represent the  $(\text{Cl}^-)$  left in the solution  $[(1.05 \times 10^{-5}) - x]$  would represent the chloride and also the silver precipitated, and therefore:

$$[.001 + (1.05 \times 10^{-5}) - (1.05 \times 10^{-5}) + x] \cdot x = 1.10 \times 10^{-10}$$

It is obvious that the value of  $x$  found by the solution of this equation differs from that calculated by the approximate method,

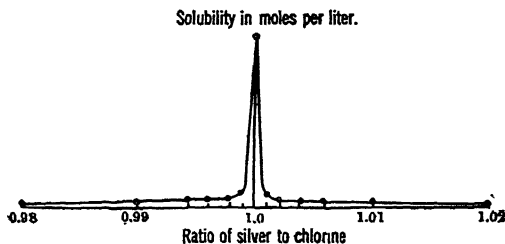


Fig. 27.—Curve showing change in solubility of silver chloride with varying ratio of silver to chlorine in mixture.

by a negligible value only, less than that resulting from the inaccuracy of the experimental determination upon which the calculation is based, namely the solubility of pure silver chloride in water.

The concentration of the ion which is not in excess is a measure of the solubility of silver chloride, and therefore the solubility of silver chloride varies with the ratio between the amounts of the two electrolytes in the mixture. It is at a maximum when this ratio is one to one and diminishes with any change in this value. These changes have been calculated for a number of mixtures and the results plotted as a graph in Fig. 27, which shows the relations between the ratio of silver nitrate to sodium chloride as abscissas, and solubility of silver chloride, as ordinates. Since

the curve represents the relation between two variables whose product is constant it takes the form of a rectangular hyperbola. It is clear that relatively greater effects are produced by the addition of small than of large amounts of excess of the reagent used as precipitating agent, and complete precipitation is never attainable.

The changes in the solubility of other precipitates which yield two univalent or two divalent ions can be calculated in a similar manner. The corresponding graphs must differ from Fig. 27 mainly in the angle of the slope between the graph and the two axes. That between the graph and the vertical axis must increase as the solubility product and therefore the solubility, if expressed in moles, increases. This means that the reduction in the solubility of the more soluble precipitates resulting from the presence of a specific percentage excess of the precipitating agent becomes less as the precipitate concerned is more soluble.

The preceding calculations involve at least three assumptions, namely, complete dissociation of all the electrolytes present, absence of complex ions, and an activity coefficient of one for all the ions concerned. These assumptions are only justifiable so long as the concentrations of all electrolytes are very small, and it is not surprising to find that the use of a very large excess of a precipitating agent may increase rather than decrease the solubility of the precipitate concerned. It was found by Jahn<sup>1</sup> that the solubility of silver chloride was decreased almost in agreement with that calculated in solutions of potassium chloride at 18° whose concentrations ranged from  $6.7 \times 10^{-3}$  to  $3.3 \times 10^{-2}$ . On the other hand Forbes<sup>2</sup> found that the solubility of silver chloride in solution of sodium, potassium, ammonium, hydrogen, calcium, strontium, and barium chlorides, of 0.933 molal strength or greater, was increased enormously above that in pure water. In solutions of sodium chloride it ranged from  $8.6 \times 10^{-5}$ , where the concentration was 0.933 to  $6.04 \times 10^{-2}$  where it was 5.039. He found that the increase was proportional to an integral power of the chloride ion and therefore concluded that the action was due to the presence of one or more complex

<sup>1</sup> Jahn, *Zeit. physik. Chem.*, 33, 454 (1900).

<sup>2</sup> Forbes, *Jour. Am. Chem. Soc.*, 33, 1939 (1911).



ions, probably  $\text{AgCl}_3^{--}$  and  $\text{AgCl}_4^{---}$ . This assumption is in accord with the theory of Abegg and Bodländer,<sup>1</sup> which assumes that many ions, especially those which possess a slight degree of affinity for their charges, show a tendency to increase this affinity by taking up unionized molecules from the solution. In this case two or three chloride ions combine with a silver chloride molecule. It seems probable that the formation of complex ions in small concentrations is a common phenomenon, and is responsible for the two effects which are of importance in quantitative analysis. In some cases it results in the formation of precipitates of abnormal composition; in others it increases the solubility of the precipitate by making it possible for the solution to attain a higher concentration of the constituent which is being separated than would be possible if only simple ions were present.

Forbes (l. c.) also calculated by interpolation that the minimum solubility of silver chloride in sodium chloride solutions should be at 0.01 molal concentration. He also found that the solubility in silver nitrate of twice molal strength was  $3 \times 10^{-5}$ . The numerous investigations on the solubility of slightly soluble substances, in solutions of electrolytes which yield an ion of the same composition as the compound with which the solution is saturated, show for the most part a fair agreement with the predictions of the solubility product principle, provided the concentrations of both electrolytes are small. The values calculated by the use of this principle should be considered ideal values toward which the actual values converge in proportion as the ideal conditions which they assume are realized.

#### Further Development of the Solubility Product Principle.

Application of the solubility product principle to precipitates which yield both uni- and divalent ions will be illustrated by calculating the solubility product of silver chromate. The solubility of this precipitate in water is 0.025 gram or  $7.5 \times 10^{-5}$  moles per liter. Since one mole of the salt yields one chromate and two silver ions,  $(\text{CrO}_4^{--})$  must equal  $7.5 \times 10^{-5}$  and  $(\text{Ag}^+)$  must be  $1.5 \times 10^{-4}$  in the saturated solution, assuming com-

<sup>1</sup> Abegg and Bodländer, *Zeit. anorg. Chem.*, 20, 453 (1899)

plete dissociation. Hence the solubility product equals  $(7.5 \times 10^{-5}) \times (1.5 \times 10^{-4})^2$  or  $1.7 \times 10^{-12}$ . It is obvious that the solubility of this salt will be affected to a greater degree by changes in  $(\text{Ag}^+)$  than  $(\text{CrO}_4^{--})$  since the former is always raised to the second and the latter to the first power in the solubility product expression.

The solubility product of precipitates which yield three uni- and one trivalent ion is calculated in a similar manner. If the solubility of such a salt, expressed in moles per liter, is represented by  $A$ , the expression for its solubility product becomes  $A(3A)^3$ . Similarly the solubility product of a precipitate which yields three di- and two trivalent ions, and whose molal solubility is  $A$ , becomes  $(3A)^3 \cdot (2A)^2$ . Larger errors should be expected in applying the solubility product principle to precipitates which yield di- or trivalent ions than to those which yield univalent ions only. The probability of incomplete ionization is greater since the dissociation takes place in stages and the value of the constants which determine each successive stage decreases rapidly. The possibility of complex formations also increases since some of the ions concerned are weaker ions. In certain cases also, more than one method of ionization is possible. Aluminum hydroxide for example may yield not only  $\text{Al}^{+++}$  and  $\text{HO}^-$  but  $\text{H}_2\text{AlO}_3^-$ ,  $\text{HAlO}_3^{--}$ ,  $\text{AlO}_3^{---}$  and  $\text{AlO}_2^-$ .

The solubility products of the precipitates listed in Table II on page 122 are given in the last column of that table. For the most part they are the values calculated by the experimenters who determined the solubilities of the precipitate concerned. In many cases the calculations assume complete dissociation and no hydrolysis; in others an attempt has been made to calculate the actual ion concentrations by estimating the actual degree of dissociation and of hydrolysis.

**Theory of Separation of Two Closely Related Ions.** The possibility of separating two ions by the addition of a reagent which is capable of forming a slightly soluble compound with both can be discussed from the standpoint of the solubility product principle. Let it be assumed that silver nitrate is slowly added to a solution containing equivalent concentrations of sodium chloride and sodium iodide. Silver iodide must begin to separate

as soon as the product of  $(\text{Ag}^+) \times (\text{I}^-)$  exceeds  $S$  where  $S$  represents the solubility product of silver iodide, and silver chloride must begin to separate as soon as the product  $(\text{Ag}^+) \times (\text{Cl}^-)$  exceeds  $S'$  where  $S'$  represents the solubility product of silver chloride. Since in the solution  $(\text{I}^-) = (\text{Cl}^-)$ , and since  $\text{AgI}$  is less soluble than  $\text{AgCl}$ , it will be the first precipitate to separate. If further quantities of silver nitrate are added more silver iodide separates and  $(\text{I}^-)$  is progressively reduced, but since  $S$  is constant the decrease in  $(\text{I}^-)$  must be associated with an increase in  $(\text{Ag}^+)$ . Both changes will progress until  $(\text{Ag}^+)$  has become so large that the solution is also saturated as to silver chloride. At this point

$$(\text{Ag}^+) \times (\text{I}^-) = S \quad \text{and} \quad (\text{Ag}^+) \times (\text{Cl}^-) = S'.$$

Since both expressions relate to the same solution  $(\text{Ag}^+)$  has the same value in both and therefore

$$\begin{array}{rcl} (\text{I}^-) & S \\ (\text{Cl}^-) & S'' \end{array}$$

This expression states that the condition for saturation with respect to both compounds is that  $(\text{I}^-)$  shall bear the same relation to  $(\text{Cl}^-)$  that  $S$  bears to  $S'$ . If still more silver nitrate is added, further quantities of both silver iodide and silver chloride must separate, but the ratio of  $(\text{I}^-)$  to  $(\text{Cl}^-)$  must remain constant. The value of this ratio can be calculated, by dividing  $1 \times 10^{-16}$ , the solubility product of silver iodide, by  $1.1 \times 10^{-10}$ , the solubility product of silver chloride, to have the value  $9 \times 10^{-7}$ .

Where the number of equivalents of silver added equals the number of equivalents of iodide ion present,  $(\text{Ag}^+)$  and  $(\text{I}^-)$  both equal  $1 \times 10^{-8}$  and the maximum concentration of  $(\text{Cl}^-)$  which could be present without causing some silver chloride to separate would be  $(1 \times 10^{-8}) \div (9 \times 10^{-7})$  or  $1.1 \times 10^{-2}$ ; that is, if the concentration of  $\text{Cl}^-$  reached the value 0.011, and if the number of equivalents of silver added equaled the number of equivalents of iodide present, the solution would be just saturated with both precipitates. An accurate separation of iodine from such a solution as the one here assumed would not be possible. Obviously one equivalent of silver would have to be added for every

equivalent of iodide ion present but even if no excess were used some silver chloride would separate if the concentration of chloride ion exceeded 0.011.

If the ratio of  $(I^-)$  to  $(Cl^-)$  in the original mixture was less than 1 : 1 silver chloride would have separated at an earlier stage in the process, even before the silver iodide; if this ratio was greater than 1 : 1 the separation of the silver chloride would be deferred. In both of these cases, however, an accurate separation of iodine from the solution would be either impossible or impracticable, as it would require that the composition of the original solution be known with a very high degree of accuracy.

**Standardization of Precipitation Processes.** The preceding discussion indicates that the solubility of precipitates in the solutions from which they are made to separate in a gravimetric determination is affected by a number of factors, and the actual solubilities cannot be calculated from the available numerical data, except with a certain degree of approximation, and then only for a few simple cases. Additional uncertainties arise from the fact that the rate at which equilibrium is attained in precipitation processes is often low, and the extent to which both the filtrate and liquid used in washing the precipitate are saturated may vary greatly with different precipitates. The actual accuracy of all such processes must be ascertained by applying it to a "primary standard," that is to some compound of the substance being determined whose chemical formula has been accurately ascertained and which is free from impurities of all kinds. It is also possible to devise a series of quantitative experiments designed to ascertain the best possible details of procedure. Such experiments should include a number of series in which systematic variations are made in (a) the ratio of sample to volume of solution used, (b) excess of precipitating agent added, (c) details of procedure in adding the reagent, (d) washing the precipitate, and (e) methods of igniting the precipitate.

## CHAPTER XI

### FACTORS AFFECTING THE PHYSICAL PROPERTIES AND PURITY OF PRECIPITATES

#### I. Theory of Formation of Precipitates

**Disperse Systems.** It is conceivable that the size of the particles of which a precipitate is composed may be reduced even to the point at which each particle consists of only a few molecules. Although it is not possible to demonstrate experimentally that the disintegration of a solid can be carried to this limit, the process of "dispersion" or "peptization," in which the size of the particle is reduced to a very small magnitude, is a well known phenomenon. If the degree of dispersion approaches the above limit, the distinction between liquid and solid becomes negligibly small. Long before the limit is reached, however, the mixture acquires a number of unusual properties. If the degree of dispersion is less, the resulting mixture is opalescent or turbid and such a mixture is called a colloid. The suspended material is then called a "sol" and, if the liquid medium is water, a "hydrosol." It was formerly supposed that only a limited number of solids were capable of forming sols and such substances were designated as colloidal. Although there is a very great difference in the ease with which different substances form sols, it seems probable that all substances possess this property to some degree, and, although the term colloidal is still used, it is more correct to speak of the colloidal form of a substance.

**Colloidal Properties.** The presence of a greatly dispersed solid in a liquid is often difficult to detect. It is not retained by the usual filtering media, and, if it settles at all on standing, settles very slowly even though its density is greater than that of the liquid because the normal effect of gravity is partly or completely

neutralized by the impacts of the rapidly moving ions present in such solutions. Such mixtures do not show turbidity or opalescence beyond a certain degree of dispersion. The hydrosols of certain substances, especially the metals, show intense and characteristic colors which vary with the degree of dispersion. This is not true of the precipitates used in analytical chemistry. The usual method of testing a mixture for a greatly dispersed solid is to pass through it a beam of light and examine it against a black background with a high-powered microscope. Each solid particle reflects some of the light and appears in the field of view as a point. It becomes possible therefore to count or photograph the number of particles and observe their movements. Even this method fails to detect particles smaller than  $6 \times 10^{-6}$  mm., which is about thirty times the size of the hydrogen molecule. When a direct current is passed through a hydrosol, the dispersed solid usually moves either with or against the direction of the current, clearly indicating that the particles are themselves charged. Apparently the colloid particles exercise a selective action for either anions or cations and become more or less definitely associated with a certain number of either, and are therefore known as positive or negative colloids. Some colloids however are either positive or negative according to the media in which they are dispersed.

**Coagulation.** Although certain colloids are stable, that is, remain in the same degree of dispersion indefinitely, others on standing become turbid or form well-defined precipitates. This represents a mere agglomeration of a number of the finer particles into larger ones. It is usually known as "coagulation" and is the converse of dispersion or peptization.

The addition of an electrolyte to a stable colloid usually causes coagulation. It may be attributed to the absorption of some of the added ions by the dispersed solid, which effects neutralization of the charge on the particles and therefore decreases or eliminates the repulsion of the particles for each other so long as they bear charges of the same sign. This suggestion finds confirmation in the fact that certain positive colloids readily coagulate certain negative colloids. The concentration of the electrolyte necessary to bring about coagulation has a fairly

definite value for colloids of the same nature and degree of dispersion. In general, divalent ions are far more effective than monovalent, and trivalent than divalent. The rate of coagulation is also increased by increasing the temperature.

**Separation of Crystalline Precipitates.** It is easily shown that certain precipitates separate at first as colloids and become crystalline on standing. It is probable that this is true of all precipitates, but that the rate at which the change takes place is so great that it is not discernible. This theory assumes that during the addition of the first drops of precipitating agent a greatly dispersed solid is formed, which coagulates as the concentration of the electrolytes present is increased, and finally the bulky "colloidal precipitate" condenses or becomes denser owing to crystallization. The time required for these changes to take place depends upon many factors. The use of colloidal precipitates is always avoided by the analytical chemist where possible, since such precipitates are invariably bulky and difficult to filter and to wash free from the associated substance which the solution contains.

**Factors Which Determine the Nature of Precipitates.** The factors which determine how far the changes described in the preceding paragraph proceed, when a precipitate is formed in solution by the chemical action between two reagents, were studied by von Weimarn.<sup>1</sup> He showed that the two important factors were the viscosity of the solution and its degree of supersaturation, that is, the ratio between the molal concentration of the separated precipitate, which is in excess of its normal solubility, assuming all of it to be in solution, and the normal solubility. He found that a given degree of supersaturation gave precipitates of about the same character even though these precipitates differed as to chemical and physical properties. By varying the degree of supersaturation he was able to prepare precipitates of barium sulfate, silver chloride, aluminum hydroxide, sodium chloride of almost any desired degree of dispersion. With solutions in which the degree of supersaturation did not exceed three, and the molal concentration did not exceed  $5 \times 10^{-5}$ ,

<sup>1</sup> Zur, *Lehre von den Zuständen der Materie* (1914).

only coarsely crystalline precipitates separated after standing for months. The very large dilution reduced the number of times within a given period in which contact between the reacting reagents as well as dispersed particles was established. Under such conditions each molecule was able to orient itself and form a structure in which all the particles were arranged according to a definite plan, that is, to produce perfect crystals of appreciable size. It also reduced the number of nuclei or centers around which crystallization could take place, and therefore resulted in the formation of a relatively small number of large crystals rather than a large number of small ones. This explains why very large crystals of such insoluble substances as quartz are common in nature, but are difficult to produce artificially. Since increasing viscosity reduces the rate of movement of the particles in the solution it should have the same effect as increasing dilution of the solution.

With a greater degree of supersaturation and larger molal concentrations, smaller but well-defined individual crystals were produced within a much shorter period of time. When the concentration was about  $3 \times 10^{-4}$  molal, the mixture became opalescent after six to eight hours and precipitation was practically complete after twenty-four hours. When the concentration was about  $2 \times 10^{-3}$ , the mixture became opalescent almost at once, and precipitation was complete within an hour. With still greater concentrations suspended colloids or hydrosols appeared at once but rather rapidly changed over into a denser aggregation of fine crystals. With a very large degree of supersaturation and molal concentration, the precipitates became at first curdy and finally gelatinous. These corresponded to the so-called amorphous precipitates, which show no evidence of being crystalline even when highly magnified, but which von Weimarn considered to be aggregates of very fine crystals. Still higher concentrations gave jelly-like masses which were extremely bulky and which exhibited the properties of emulsions rather than those of mixtures of solids and liquids.



## II. Contamination of Precipitates

**Adsorption.** This term was first used by E. du Bois Raymonds to represent the retention of soluble substances by powders or porous solids when placed in solutions of such substances. A typical illustration is the well-known property of bone charcoal of removing coloring matter from solutions containing certain coloring matters. The facts clearly indicate that an attractive or restraining force is exerted by the solid, which tends to hold a layer of the molecules of the adsorbed substance, which probably does not exceed the thickness of a single molecule, at the surface of the solid, and either delays or entirely prevents the removal of that substance by washing. It seems probable that such forces exist at the surface of all solids because the attractive forces of the component elements are not so fully satisfied at the surface as within the mass of the solid. Similar phenomena in which gases are adsorbed by solids have been studied exhaustively. Since the action is purely a surface action, its magnitude should be increased by increasing the surface as compared with the volume of the solid, and therefore by decreasing the size of the particles of which the mass is made up. This is in agreement with an enormous amount of experimental evidence.

Adsorption is a distinctly selective process and varies enormously with the chemical properties of both the solid and the soluble substance which is adsorbed, but the selective nature of the process has not been correlated with any of the other properties of the substances concerned.

Adsorption also depends upon the concentration of the liquid phase with respect to the substance adsorbed, but is not proportional to the concentration. The amount of a specific substance adsorbed by a solid which has the same physical and chemical properties can in many cases be expressed with a fair degree of accuracy by the formula

$$A = K \cdot C^{1/n},$$

in which  $A$  is the amount adsorbed per unit weight of solid,  $K$  is the selective constant, and  $n$  is a constant which is always greater than unity and frequently has the value not differing greatly from two.

**Occlusion.** The contamination of precipitates with substances derived from the solution from which they separate is a very general phenomenon and there is reason to believe that it is not always due to adsorption. Certain solids are capable of dissolving large amounts of other solids and forming solid solutions, and it is probable that many precipitates are capable of dissolving small amounts of a number of substances. If so, it is obvious that the dissolved impurity cannot be removed without dissolving the precipitate itself.

There is also reason to believe that impure precipitates may arise through the formation of small amounts of a variety of complex compounds or basic salts along with the precipitate of normal composition. It is a well-known fact that if barium sulfate is precipitated from a solution containing ferric ion the resulting precipitate always contains appreciable amounts of ferric iron, even though the precipitate has been very carefully washed. The weight of ignited precipitate obtained, when iron is present, is less than the weight which should have been obtained if all the sulfate ion in the solution were converted into barium sulfate. This has been explained<sup>1</sup> by assuming that the precipitate was contaminated with small amounts of a double sulfate of iron and barium. Although such a compound has not been actually separated a number of double salts containing ferric sulfate are known. If the compound has the formula  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{BaSO}_4$  it should be expected to yield one mole of ferric oxide and one of barium sulfate when ignited. Although there is a gain of one molecule of ferric oxide this is much less than the loss due to the volatilization of three molecules of sulfur trioxide, which should have formed three molecules of barium sulfate.

Further suggestions based upon the assumption that the partial ionization of uni-divalent electrolytes may yield insoluble compounds of abnormal composition have been made. The presence of chlorides and nitrates in precipitates of barium sulfate which have separated from solutions containing chloride or nitrate ion has been attributed to the presence of  $\text{BaCl}^+$  and  $\text{BaNO}_3^+$ , which might be assumed to form  $(\text{BaCl})_2\text{SO}_4$  and  $(\text{BaNO}_3)_2\text{SO}_4$ ,

<sup>1</sup> Jannisch and Richards, Jour. prakt. Chem., 39, 321 (1889).

assuming of course that the solubility of these substances in the solution concerned was sufficiently small.<sup>1</sup> The terms adsorption and occlusion have been used somewhat loosely. The term occlusion is more general and in this book will be used to designate the contamination of precipitates without implication as to the nature or the cause of the phenomenon.

/ **Factors Affecting Occlusion.** In order to gain a more concrete idea of the errors resulting from occlusion a number of experimental results will be discussed. In these experiments barium sulfate was made to separate from solutions containing potassium nitrate. Twenty-five cc. of a solution of sulfuric acid, containing exactly 0.425 gram of  $\text{H}_2\text{SO}_4$ , which should yield exactly 1.0118 grams of  $\text{BaSO}_4$ , were used. Variable amounts of potassium nitrate were added in the different experiments, but the solution was in every case diluted to 200 cc., heated to boiling, and the  $\text{BaSO}_4$  precipitated by the addition of 50 cc. of a solution containing 1.30 gram of  $\text{BaCl}_2$ . After standing for sixteen hours the precipitate was filtered off, thoroughly washed, ignited, and weighed. The results obtained were as follows:

Series No.	1	2	3	4
Weight $\text{KNO}_3$ present.....	0.0000	1.0000	2.0000	5.0000
Weight of precipitate found (A).....	1.0131	1.0199	1.0308	1.0476
Weight of precipitate found (B).....	1.0134	1.0160	1.0291	1.0468
Average of A and B.....	1.0133	1.0180	1.0300	1.0472
Excess of weight found.....	0.0015	0.0062	0.0182	0.0354

A qualitative examination showed that the precipitates obtained in the first series contained very small amounts of chlorides; those obtained in the other series gave an alkaline reaction. It is probable that the 1.5 mg. in excess of the theoretical weight obtained in the first series represented occluded barium chloride, and the much larger excesses in the other series represented barium oxide, which resulted from the decomposition of barium nitrate occluded by the precipitate.

<sup>1</sup> Halett and Duschak, *Zeit. anorg. Chem.*, 40, 196 (1904).

Experiments in which soluble salts were added to a mixture in which a precipitate had already separated, designed to ascertain whether occlusion can take place after, as well as during, the separation of the precipitate, have given variable results. In all cases, however, the amount of occlusion thus found was very much less than that to be expected if the added substance had been present during the separation of the precipitate. Obviously the results of such experiments would depend upon the cause of the occlusion in each case; it would be least if due to the formation of solid solutions.

Among other factors which should be expected to affect the amount of occlusion are the order in which the two reagents are mixed. If reagent A is added to reagent B the latter will in general be in excess in the resulting mixture up to the time at which an equivalent amount of A has been added; if reagent B is added to A reagent A will be in excess. The former set of conditions would favor the occlusion of B more than A, the latter of A more than B. It is impossible, however, to insure an absolutely uniform distribution of the two reagents throughout the mixture during the time they are being mixed. There is a pronounced tendency for both reagents to exceed temporarily the average concentration of the mixture in certain portions of the mixture. Hence some of the precipitates may separate in the presence of a concentration much greater than the average concentration of one reagent or the other, and the effect of mixing the two reagents in the predetermined order may be greatly diminished. Owing to the difficulty of obtaining absolutely identical conditions with respect to these factors, decided differences in the amount of occlusion may result, even when an attempt to make precipitations under identical conditions is made.

**Dependence of Occlusion upon the Specific Properties of Ions.** The results of experiments, in which the amount of occlusion was determined when a certain precipitate was made to separate from solutions containing equivalent amounts of different electrolytes containing a common ion, show that the presence of certain ions invariably results in a large amount of occlusion. The much larger tendency for the occlusion of nitrate than

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of chloride ion by barium sulfate was shown in a series of experiments, made under the same conditions as those already quoted, except that amounts of either chlorides or nitrates sufficient to yield equal concentrations of chloride and nitrate ion respectively, were also present.

Series No.	5	6	7	8
Salt added....	0.0000	0.37HCl	0.59NaCl	0.75KCl
Wt. of ppt. A..	1.0131	1.0135	1.0088	1.0054
Wt. of ppt. B..	1.0134	1.0143	1.0103	1.0064
Avg. A and B..	1.0133	1.1139	1.0096	1.0059
Error.....	+0.0015	+0.0021	-0.0022	-0.0059

Series No.	9	10	11	12
Salt Added....	0.54(NH <sub>4</sub> )Cl	0.56CaCl <sub>2</sub>	0.48MgCl	0.0000
Wt. of ppt. A..	1.0080	0.9954	1.0140	1.0136
Wt. of ppt. B..	1.0091	0.9961	1.0155	1.0137
Avg. A and B..	1.0086	0.9958	1.0148	1.0137
Error.....	-0.0032	-0.0160	+0.003	+0.0019

Series No.	13	14	15
Salt added....	0.63HNO <sub>3</sub>	0.85NaNO <sub>3</sub>	1.0KNO <sub>3</sub>
Wt. of ppt. A..	1.0376	1.0368	1.0308
Wt. of ppt. B..	1.0400	1.0413	1.0291
Avg. A and B..	1.0388	1.0391	1.0300
Error.....	+0.0270	+0.0273	+0.0182

Series No.	16	17	18
Salt added....	0.8(NH <sub>4</sub> )NO <sub>3</sub>	0.82Ca(NO <sub>2</sub> ) <sub>3</sub>	0.73Mg(NO <sub>3</sub> ) <sub>2</sub>
Wt. of ppt. A..	1.0244	1.0144	1.0339
Wt. of ppt. B..	1.0238	1.0174	1.0330
Avg. of A and B	1.0241	1.0159	1.0335
Error.....	+0.0123	+0.0041	+0.0217

By comparing the entire series of results in which chlorides were present with the series in which equivalent concentrations of nitrates were present, it is apparent that the substitution of nitrate for chloride ions increased the total weight of precipitate found by an approximately equal amount. The very high results obtained when even moderate amounts of most of the nitrates used were present are evidently due to the fact that the precipitates contained nitrates in addition to barium sulfate, either as the result of adsorption or the formation of complex compounds or solid solutions. A further study of these results indicates that there are decided differences in the extent to which the metallic ions are occluded. The introduction of sodium, potassium, ammonium, and calcium ions reduced the positive errors, resulting from the presence of equivalent concentrations of chloride and nitrate ions necessarily added at the same time, and, where chloride ion is present, the negative errors exceed the positive errors, and the net results are low. This may be due to adsorption or to the formation of double salts such as  $\text{BaSO}_4 \cdot \text{Na}_2\text{SO}_4$ , in which a metal having a smaller atomic weight than barium is substituted for that element. The results obtained in the experiments in which hydrogen and magnesium ions were added are not so conclusive. In general there is a very slight increase in the weights of precipitates obtained, but these increases are not greatly different from those which might properly be attributed to the chloride and nitrate ions also present. Some work by other experimenters<sup>1</sup> has shown that the presence of moderate concentrations of hydrogen ion gives slightly low results, possibly owing to the formation of an acid sulfate of barium.

A more conclusive method of estimating the extent to which the different anions are occluded would involve an actual determination of the amounts of anions found in the separated precipitates by use of the proper analytical methods. This procedure was used in studying the occlusion of anions when barium sulfate was made to separate from a solution of sodium sulfate by the addition of barium chloride. It was found<sup>2</sup> that the tendency for the

<sup>1</sup> Allen and Johnston, *Jour. Ind. and Eng. Chem.*, 2, 199 (1910).

<sup>2</sup> Wieser and Sherrick, *Jour. Phys. Chem.*, 23, 207 (1919).

occlusion of the more common ions expressed in a series of decreasing numerical values, was ferrocyanide, nitrate, nitrite, chlorate, permanganate, ferricyanide, chloride, bromide, cyanide, and iodide. This order is of significance only in the precipitation of barium sulfate.

**Method of Avoiding Error from Occlusion.** The preceding paragraphs make it clear that it is not possible to predict the probable error resulting from occlusion in any specific determination, or even whether the error will be positive or negative; such information can only be obtained by an actual experiment. They also indicate that it is a phenomenon which should be expected until the contrary has been proved, and therefore the presence of any additional substance in the solution from which a precipitate is to be separated should be avoided. Furthermore, whatever theory as to the nature of the process of occlusion is adopted, the magnitude of the effect diminishes with diminishing concentration of the occluded substances. If a substance is but slightly occluded, the error can often be reduced to negligible proportions by precipitating from a sufficiently diluted solution, although it would not be advisable to dilute too much owing to the increased error from the solubility of the substance precipitated. The negative error from solubility may be made to counterbalance a positive error from occlusion if all the specifications for the process have been correctly formulated.

In other cases it may be preferable to eliminate the objectionable substance by evaporation, or by precipitation, or by conversion of it into a form which is less subject to occlusion. Thus the nitrate ion, which is so objectionable in the determination of sulfate ion, can be eliminated by evaporating with an excess of hydrochloric acid; similarly the ferric ion may be precipitated and filtered off, or it may be reduced to ferrous ion, which is occluded but slightly, or it may be converted into a complex ion by the addition of oxalic acid. Such procedures necessarily demand that the reagent added can be readily removed or be less objectionable than the original substance.

A third remedy is to purify the precipitate containing the occluded substance by redissolving and reprecipitating, that is to use a "double precipitation." The theory of this procedure is

that the second precipitation is made in the presence of a much smaller concentration of the occluded substance than the first. It is frequently impossible to find a solvent which dissolves the precipitates readily without introducing large concentrations of other ions which are also largely occluded.

### III. Classification of Precipitates

**Basis of Classification.** The work of von Weimarn and others discussed on page 134 shows that the physical form of a precipitate may be made to vary between that of coarse crystals and a jelly by varying the degree of supersaturation of the solution from which it separates. The conditions of analytical work, however, impose limits upon the possible range of variation in the degree of supersaturation attainable because it is necessary to work with solutions the volume of which is neither immoderately large or small, and with amounts of precipitates which can be separated and weighed without large percentage errors. The range of variation in the form of the precipitates actually obtained in analytical work is therefore limited — the limit for each precipitate depending largely on its solubility. It is convenient therefore to classify precipitates with respect to the form which they ordinarily assume when separated within the range of conditions commonly used in analytical work. Obviously it is not possible to define accurately the limits of each class.

**Crystalline Precipitates.** These may be defined as those which are made up of particles bounded by surfaces which can be recognized as plane when examined with moderate magnification, or which reflect light, or show a peculiar silky sheen when observed in the associated liquid. They are the most soluble of all the precipitates used in analytical work and frequently contain water of crystallization. They include  $\text{PbCl}_2$ ,  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6 \text{H}_2\text{O}$ ,  $\text{Zn}(\text{NH}_4)\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{KClO}_4$ ,  $\text{K}_2\text{PtCl}_6$ . They are distinguished as a class by their tendency to form supersaturated solutions from which the normal amount of precipitate separates but slowly. This sometimes makes it desirable to use mechanical



shaking devices in order to reduce the time needed to a minimum. Their large solubility makes it necessary in some cases to add alcohol or some other reagent by which the solubility is reduced. They are easy to filter and wash, however, and rarely adsorb or occlude other substances to a large extent.

**Pulverulent Precipitates.** These, as the name implies, are fine powders, but actually consist of fairly dense aggregates of fine crystals. They include such substances as  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$ ,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MoO}_3 \cdot 3 \text{H}_2\text{O}$ . The individual particles are sometimes so small as to make it difficult to retain them on a filter, but this difficulty is usually avoided by adopting conditions which insure the formation of a limited number of crystal nuclei and opportunity for the growth of the particles formed. The large surface they expose in some cases leads to rather large errors from occlusion and possible losses from "creeping," that is, movement by capillary action of the fine particles over the side of the filter above the level of the liquid which it contains.

**Curdy Precipitates.** These result from the coagulation of hydrosols without condensation to the granular aggregates of pulverulent precipitates. They include  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{Ag}_2(\text{CN})_2$ ,  $\text{AgCNS}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{CuI}$ ,  $\text{CuCNS}$ . Complete coagulation is usually effected with but little difficulty, in the presence of sufficient amounts of electrolytes, by heating and vigorous stirring. The ease with which they are peptized makes it necessary to avoid washing with large amounts of water which contains no electrolytes. Their solubility is small but there is little tendency for them to separate in a form which is difficult to filter and wash.

**Colloidal Precipitates.** These are very slightly soluble precipitates, which first form hydrosols and coagulate with the formation of very bulky flocculent or jellylike masses. They include  $\text{Al}(\text{HO})_3$ ,  $\text{Cr}(\text{HO})_3$ ,  $\text{Fe}(\text{HO})_3$ ,  $\text{Si}(\text{HO})_4$ ,  $\text{Ti}(\text{HO})_4$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{CuS}$ , and  $\text{ZnS}$ . The formulae given are the ones usually attributed to these substances but it is probable that they are hydrated to a greater degree than these formulae indicate. They are all extremely bulky and difficult to wash, and the amounts which can be handled in a quantitative process are small. The more jelly-like precipitates such as  $\text{Al}(\text{HO})_3$  and  $\text{Si}(\text{HO})_4$  act almost as

though the component masses possessed a definite structure, which is not easily disintegrated even by stirring. The diffusion of liquids through such a substance is necessarily a slow process which greatly increases the difficulty of filtration. Filtration with suction usually yields a still more impervious jelly-like film and retards rather than hastens the rate of filtration.

## CHAPTER XII

### MECHANICAL DETAILS OF PRECIPITATION PROCESSES

**Media Used for Filtration.** The separation of precipitates from liquids is essentially a process of straining, in which the solid particles are separated from the liquid by the use of a porous diaphragm. These diaphragms can be made from a variety of media and differ greatly as to efficiency and adaptability to different purposes. Cellulose, either in the form of a pulp or of a paper of open, loose texture, has many advantages. Since it is usually associated with small amounts of inorganic salts and silica, which may be dissolved to some extent by the liquid filtered through it, these substances should be removed as far as possible by digesting it with both hydrochloric and hydrofluoric acids before it is used for quantitative work. Properly prepared cellulose should not contain more than 0.01 per cent of non-combustible matter. It is not appreciably acted upon by solutions of salts, or strong acids whose concentrations are less than 6 normal, or strong bases whose concentration does not exceed 0.2 normal. Higher concentrations of these reagents cause it to become gelatinous and useless as a filtering medium, and at still higher concentrations to form glucose and a variety of decomposition products. Especially prepared papers, which vary greatly as to thickness and texture, are to be obtained from dealers; those of loose and porous character permit of rapid filtration, but are unable to retain the finest precipitate; the more compact forms are more efficient but slower.

Asbestos, or mineral wood, unlike cellulose, is non-combustible and should be only slightly hygroscopic. Different grades of the mineral differ greatly as to freedom from associated minerals, length of fiber, and the ease with which they can be reduced to a satisfactory pulp. The best is the white long-fibered variety,

which can be properly disintegrated either by scraping with a knife-blade while dry or by triturating in an agate mortar while wet. It should also be digested with strong hydrochloric acid before use in order to decompose any other minerals which might be dissolved during its use as a filter and thereby change the weight or contaminate the resulting filtrate. As it cannot be made into a satisfactory fabric which can be used like filter paper, it must be supported on a perforated disk of platinum or porcelain, or on a crucible which has a perforated bottom. If the precipitate is to be weighed on the filter, care must be taken to wash the latter with at least 100 cc. of water to remove loosely adhering fibers, which might be washed away during its use as a filter and thereby change the weight. If a beam of light is made to pass through the filtrate it will invariably show small amounts of suspended asbestos fibers. If a high degree of accuracy is demanded, the filtrate should always be run through a paper filter, the latter burned, the residual asbestos weighed, and the weight found added to the weight of the crucible and precipitate. This correction is usually less than a milligram. It is further desirable always to use the minimum amount of asbestos in preparing the filter mat, for, owing to its relatively large surface area, the errors from varying amounts of moisture condensed on it may become appreciable. A mat which is 1 mm. thick after drying, and which if distributed over a disk 1 cm. in diameter, does not weigh more than 0.300 gram, is entirely satisfactory unless the precipitate is unusually fine. A disk of platinum or porcelain placed on top of the mat reduces the needed thickness.

Glass wool is sometimes used in the same manner as asbestos. As the fibers of which it is composed are more elastic and pack together less compactly it is not so readily made into a filter of equal efficiency.

Platinum sponge, which is easily prepared by reducing the salts of that element to the metallic state, is also used like asbestos but its cost makes it necessary to recover it after use by dissolving the associated precipitate and washing till free from the resulting salts.

Alundum, or fused aluminum oxide, when crushed to a fine powder, can also be made into an efficient filter and has the

advantage of being unaffected even by strong acids and bases. It is usually mixed with a small amount of cementing material and moulded into the form of crucibles or cylinders. In using these crucibles some difficulty is experienced in washing them free from soluble salts after each filtration.

#### Devices for Filtering When the Precipitate is Not to be Weighed.

In discussing the devices used for filtration we can distinguish between those cases in which the precipitate is to be weighed at once and those in which the separation is only one of the pre-



Fig. 28.—Funnel for rapid filtration.

liminary operations which precede the actual determination of the desired substance. In the latter case the precipitate may be discarded entirely, or it may again be brought into solution by treatment with other reagents and the desired substance can be separated from the resulting solution by further operations. Several devices can be employed. The simplest consists of a paper filter, supported on a glass funnel. The rate at which a liquid passes through such a device depends, aside from the character of the filter paper, upon the nature and amount of the precipitate, and the viscosity of the associated liquid. It can be increased by lengthening the stem of the funnel or by attaching to the latter a piece of tubing having the form shown in Fig. 28. The rate of filtration is then increased in proportion to the length of the column of liquid which the filter

contains. The chief difficulty in using this device is to keep the tube full of liquid. If the filter is not made to fit the funnel exactly air may be drawn into the tube from above. Since the angle of the funnels in general use is  $60^\circ$  the filter should fit the funnel if folded twice along diameters at right angles to each other; actually it is often necessary to make the second fold at a slightly different angle. If the surface of the tube is not perfectly clean, or if its diameter is too great, the liquid which passes the filter may fail to fill the tube completely. The surface can usually be kept in proper condition by rinsing with either a strong solution of sodium hydroxide or with the acid-chromate mixture. Reducing the diameter of the

tube reduces the rate of filtration owing to the greatly increased effect of surface tension. By bending the tube near its upper end through a complete circle, as shown in the figure, a tube of larger diameter than would otherwise be possible can be used. If the tube is made too long and acts efficiently, sufficient pressure may be developed to cause the filter to break at the apex of the funnel where it is entirely unsupported. It is sometimes necessary therefore to introduce a support in the form of a cone made of perforated platinum to fit the apex of the funnel. If the paper filter is used, some of the precipitate, especially if the latter is finely divided, is carried into the pores of the paper; and if it is desired to bring this precipitate into solution, or to treat it with other reagents, a large volume of the reagent must be poured through the filter or the latter must be transferred to another vessel, opened out, and digested with the reagent. This usually consumes much time, requires the use of an undesirably large volume of reagent, and the cellulose of the filter may be acted upon by the reagent which it is desired to use.

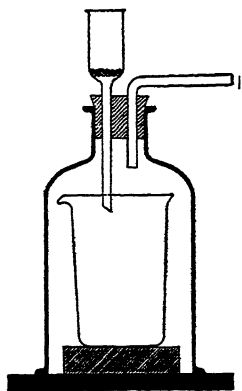


Fig. 29.—Filtration by use of a glass filtering tube.

These difficulties are avoided by the use of an asbestos filter in which a Witt filter plate is used to support the asbestos mat in the bottom of a "filtering tube" as shown in Fig. 29. In this and all devices in which asbestos pulp is used, suction greater than that easily obtained by increasing the length of the funnel stem is necessary. The stem of the filter tube passes through a rubber stopper, which closes the upper end of a bell jar, and into a beaker which retains the filtrate and washings. An air-tight joint between the bottom of the bell jar and the supporting glass plate is maintained by the use of a mixture of wax and vaseline, and the air sucked out by means of a second tube passing through the rubber stopper which is attached to a pump. This device permits of extremely rapid filtration and by varying the thickness and texture of the asbestos layer precipitates of any desired degree of fineness can be retained. After filtration the filter and

adhering precipitate can be completely transferred to another vessel and dissolved by any desired reagent, after which the residual asbestos can be removed by a second filtration.

**Devices for Filtration When the Precipitate is to be Weighed.** If the separated precipitate is to be weighed it must be freed from water and sometimes it must be strongly ignited in order to change it into a pure compound having a known composition. It is desirable therefore that the medium used for filtration shall have such properties that it can be treated exactly as the precipitate is treated without danger of affecting changes in its weight, and that the filter shall be of such a form that it can be easily ignited and accurately weighed both before and after the precipitate has been separated upon it.

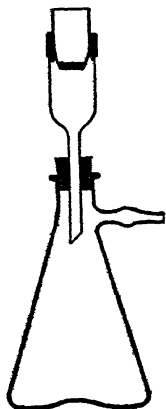


Fig. 30.—Filtration by use of a Gooch crucible.

Asbestos, glass wool, and platinum sponge can be ignited without undergoing appreciable changes in weight and do not react with the precipitates ordinarily used when ignited with them. The most convenient form of filtering device, in which these media are used, is the Gooch crucible. Its bottom is pierced by a number of fine holes; it is connected with an adapter or filtering tube by means of a rubber band, and the filtering tube connected with a filter flask by means of a rubber stopper as shown in Fig. 30. If the asbestos mat is properly prepared, and an efficient pump is available, this device gives efficient and extremely rapid filtration. The same crucible may be used for the separation of a number of precipitates without changing the asbestos mat.

If it is not necessary to heat the precipitate after filtration to more than  $350^{\circ}\text{C}.$ , a glass filter tube, similar to the one represented in Fig. 29, which is used in conjunction with a Witt filter plate, or platinum cone, can be used to advantage.

A crucible of alundum has many of the advantages of a Gooch crucible, but some difficulty is experienced in washing it free from soluble salts and fine particles of precipitate after repeated use.

**The Transfer of Precipitates.** The transfer of a precipitate from the vessel in which it has been made to separate involves possibilities of large losses and corresponding errors in the final result. Most of it is easily rinsed out of the retaining vessel, but it is well to assume that some of it always adheres to the walls of the vessel more or less tenaciously. If the precipitate is fairly soluble and has been permitted to separate slowly much of the surface may be coated with a layer of fine crystals which are difficult to rub off. If the precipitate is of a gelatinous nature it may form a thin but closely adherent film. It is therefore always advisable to go over the entire inner surface of the vessel with a rubber-tipped rod, commonly known as a policeman, for the purpose of loosening up the adherent particles. The transfer of the suspended precipitate is effected by use of a stream from a wash bottle, similar to that represented in Fig. 31. It should be provided with a flexible joint at *A* by means of which the stream of water may be directed as desired, and one or more easily detachable nozzles by which the size of the stream can be varied. The delivery tube is bent at *B* in order to permit of a more complete expulsion of the water when the flask is held in an inclined position. In transferring a mixture of a liquid and precipitate from one vessel to another, the mixture should always be made to run down a glass rod or policeman. If the rod is kept perfectly vertical and the lip of the beaker held against it while the liquid is being poured out, and the beaker turned till its side is also nearly vertical before the lip is removed from the contact with the rod, none of the liquid will run down the side of the beaker and the transfer can be made without any loss whatever.

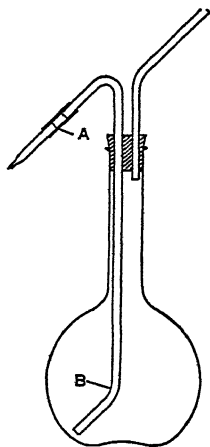


Fig. 31.—Wash bottle.

**The Theory of Washing Precipitates.** The precipitate finally separated on the filter is contaminated with various soluble substances present in the solution associated with it. If these



substances are easily volatilized during the subsequent ignition, and if they do not react with the precipitate in such a manner as to give rise to volatile compounds with the precipitate during the ignition, their removal is not necessary. In the great majority of cases both of these conditions are not complied with, and the precipitate must be washed with an appropriate liquid, the amount of which should be made as small as possible, owing to the solvent action of the liquid on the precipitate.

The efficiency of the method used in washing precipitates is readily calculated if ideal conditions only are considered. If  $A$  represents the weight in grams of the impurity to be removed, and  $V$  the volume in cubic centimeters of the wash solution added, and if it is assumed that the filter is in all cases allowed to drain until only 1 cc. of liquid remains in contact with it, and that there is an equal distribution of the soluble salt throughout the volume of liquid used, each washing would remove  $\frac{V}{V+1} A$  grams

of the impurity and leave  $\frac{1}{V+1} A$  grams behind. The general expression for the amount of impurity left on the filter after  $n$  treatments is  $\left(\frac{1}{V+1}\right)^n A$ . If, for example, the amount of impurity to be removed was 0.2 gram and the precipitate was washed four times with 9 cc. of solution under the conditions named above, only 0.00002 gram would remain, an amount which can be safely neglected.

The formula further shows that the efficiency of the process decreases greatly as the volume of the liquid left in contact with the precipitate increases, and that the use of several portions of wash solution of small volume is decidedly more effective than the use of a smaller number of large portions. If the 36 cc. of wash solution used in four equal portions in the above named example had been used as a single portion the weight of impurity still left in the filter would amount to 0.0054 gram.

**Discrepancy between the Theory and Practice.** Experience does not agree with the predictions of the theory outlined above, and the assumption that the impurities are equally distributed

throughout the wash solution is not valid. When the latter is merely poured through the filter it may not remain in contact with the precipitate long enough to bring about a uniform distribution of the soluble salts, and it is often difficult to prevent the formation of channels in the mass of precipitate, especially where the latter is of a gelatinous character, which prevents the solution from coming into intimate contact with the soluble impurities. The only reliable method of procedure is to wash the precipitate until an actual test of the washing shows that soluble substances are no longer being removed in appreciable amounts. It is often convenient to ascertain this by evaporating a reasonably large volume of the last washings (at least 20 cc.) to complete dryness and noting the amount of residue left. In other cases it is more convenient to test the washings for the compound which is being removed by an appropriate and sufficiently delicate qualitative test. It is usually safe to assume, however, that precipitates which have been brought down under identical conditions from solutions of the same composition require the same amount of washing, and in repeating quantitative processes much unnecessary labor can be avoided by ascertaining the amount of washing necessary in the first determination.

**Washing by Decantation.** It is desirable to wash precipitates which rapidly clog up the pores of the filter in the original vessel, that is, to avoid bringing them on the filter as far as possible until the impurities have been removed. This can be effected by allowing the precipitate to settle to the bottom of the vessel, "decanting" off the clear supernatant liquid through the filter, adding wash water, stirring and repeating the cycle of operations as long as may be necessary. The separation of precipitates of low density is often an extremely slow process, and where they are also bulky, comparatively large amounts of solution must be left in contact with the precipitate after each decantation. On the other hand, the wash solution remains in contact with the entire precipitate long enough to insure an equal distribution of the soluble impurity throughout its volume. On the whole the process of washing by decantation is slow but with certain types of precipitates it is the best method to employ.

**Ignition of Precipitates.** The precipitate finally separated is necessarily wet and must be dried before it can be weighed. Frequently it is retained on a paper filter, which must be burned up; and it often consists of a mixture that must be converted into a compound which has a definite composition. All of these changes represent gas-evolution processes; therefore, precipitation processes involve the use of the principles discussed in Chapter VI.

The chief difficulty encountered in igniting precipitates which have been separated on a paper filter is the partial reduction which they may undergo through the action of the carbon monoxide and volatile hydrocarbons formed during the decomposition of the paper. This difficulty is largely eliminated by adopting the following procedure.

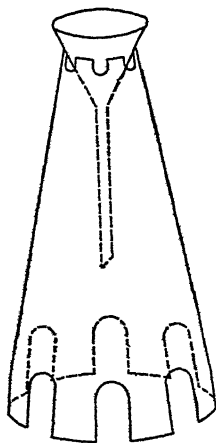


Fig. 32.—Support for drying filter.

*First*, the filter is dried at a temperature of  $100^{\circ}\text{C}$ . or less in order to make it possible to separate the greater part of the precipitate from the filter while it is being destroyed. This is conveniently effected by placing the funnel containing it in a support similar to that shown in Fig. 32 and heating on a hot plate or sand bath.

*Second*, the filter is removed from the funnel, inverted over a clean, dry watch-glass which rests on a piece of glazed paper, and the precipitate is detached and transferred to the watch glass without loss by crumpling slightly between the fingers.

*Third*, the filter is made into a compact roll and dropped into the crucible in which the ignition is to be made, and heated cautiously until all volatile matter has been "smoked off"; the temperature is then raised to redness, and the heating continued until the residual carbon is entirely consumed. Obviously these operations should be carried out in a good supply of air, and hence the crucible should be supported on the triangle in an inclined position and the flame allowed to play against its bottom only.

*Fourth*, the precipitate temporarily set aside is transferred without loss to the crucible by means of a camel's-hair brush, which requires careful manipulation.

*Finally*, the crucible is heated under whatever conditions are necessary to convert it into a pure substance of known composition. This may require heating in a current of some particular gas.

## CHAPTER XIII

### THEORY OF ELECTROLYTIC PRECIPITATION

#### I. Factors Determining the Voltage Required

**Precipitation by Electrolysis.** Certain elements are more easily and accurately determined when precipitated by means of an electric current than when precipitated by reagents. These elements include (a) certain metals which are easily reduced to the metallic state from their ions, (b) certain other metals whose ions are easily changed into insoluble oxides, (c) certain anions which form insoluble compounds with the metals of which the anode is composed. In discussing the accuracy and advantages of such processes three important considerations should be kept in mind, namely, the completeness of the precipitation, the purity of the precipitate, and the time required.

**Nature of Electrolysis.** The passage of an electric current through an electrolyte is always associated with chemical action at both electrodes, oxidation of one or more components of the solution or of the electrode at the anode and a corresponding reduction at the cathode. These changes are necessarily associated with a particular direction of transmission. If, according to the older usage, the direction of the current is defined as the direction of flow of positive charges, the current enters the solution by the anode and leaves it by the cathode. It is much more logical to correlate the direction of flow with the movement of the electrons, which reverses this order.

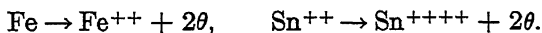
Assuming that the electrolytes in solution are already in equilibrium, the process of electrolysis is associated with a consumption of energy, and the sum of the changes in free energy of all reactions which take place must have a positive value which corresponds to the expression

$$\Delta F = \frac{-N \cdot F \cdot E}{4.185},$$

in which  $\Delta F$  is the free energy change in calories; N is the number of equivalents of chemical change effected at both anode and cathode; F is the value of the faraday, namely 96,500 coulombs; and E, which in this case must have a negative value, is the minimum voltage needed for the change. The free energy of an oxidizing-reducing process, which takes place spontaneously, must be capable of yielding, rather than requiring the expenditure of electric energy and therefore demands a negative value for  $\Delta F$  and a positive value for E. The minimum voltage required depends upon the changes at both anode and cathode, but it is obviously simpler to consider these separate electrode or half-cell reactions and then combine them as needed rather than be obliged to consider the very large number of possible combinations separately.

**Electrode Potentials.** The process taking place at the anode involves oxidation and passage of electrons to the external or metallic circuit; that at the cathode involves reduction and removal of electrons from that circuit. Frequently the reduction process at the cathode may, under other conditions, be made to take place in the reverse direction, that is, to involve oxidation, and it is logical to conceive of all reduction processes as being reversible. There is a decided advantage in considering all processes taking place at both electrodes as actual or possible oxidation processes. The number of oxidation processes represented by electrode reactions is large and they vary greatly as to their nature. They may be expressed by means of reactions, in which  $\theta$  is used to represent the electron, and classified as follows.

1. Increase in the positive charges associated with the substance oxidized, such as:

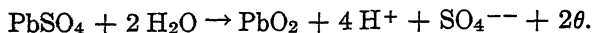


2. Decrease in the number of negative charges associated with the substance oxidized, such as:

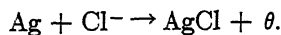


3. Decomposition\* of water with liberation of oxygen and formation of hydrogen ion, that is, an increase in the valence of oxygen from -2 to zero.

4. Decomposition of water with formation of hydrogen ion and oxidation of some other substance by the oxygen rendered available, such as:



5. Oxidation of the metal of the electrode with formation of an insoluble substance, such as:



All processes involving oxidation can be thought of as the result of an inherent tendency on the part of some substance to yield free electrons and form one or more new substances. The intensity of such processes varies greatly and can be measured by the difference of potential between the metal electrode and the solution with which it is in contact. This is known as the electrode potential. Direct measurement of the actual values of these potentials is not possible, but it is not difficult, in many cases at least, to measure the difference in potential between such electrodes by measuring the electromotive force required in a series of processes in which some one electrode is made either anode or cathode. Such measurements are valueless unless certain requirements are complied with. They must represent single definite reactions, which are easily reversed, and must be so carried out that the amount of current flowing through the cell is negligibly small. As a standard of comparison the normal hydrogen electrode has many advantages. The reaction which takes place is an easily reversible process represented by the equation



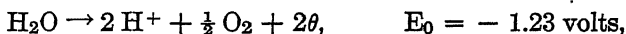
Since hydrogen gas does not have the properties of a metallic conductor it must be used in association with a strip of metal like platinum or iridium which is not acted upon by the solution used and which is capable of dissolving hydrogen. The electrode in common use is represented in Fig. 33 and consists of a piece of platinum coated with finely divided platinum. This electrode

is in contact with a stream of pure hydrogen gas and with a solution containing a molal concentration of hydrogen ion. The potential difference assigned to this electrode is zero and those substances which are more easily oxidized than hydrogen must have positive values for their electrode potential, while those which are less easily oxidized must have negative values.

**Use of a Table of Electrode Potentials.** A table giving the difference, in volts, between the potentials developed when certain reactions take place and that developed by the standard hydrogen electrode will be found on page 160. The values given assume that the reactions take place at standard conditions and are designated by the symbol  $E_0$ . Such a table has many uses. At present we are concerned with it as a source of data from which to calculate the minimum potential difference required to cause a desired chemical process to take place. Such processes necessarily require that one of the two electrode reactions takes place in the reverse direction from that given in the table, but the corresponding electrode potential for the reversed process is simply that given in the table with its signs changed. For the reaction



the two processes are



and



The minimum voltage for the entire reaction is therefore  $-0.886$ , that is, a potential difference of  $0.886$  volt must be used to cause the reaction to take place. It must be kept in mind however that the values found by such calculations are valid only when the temperature, the concentration of active reagents in the liquid phase, and the pressures of the gases in the gas phase are

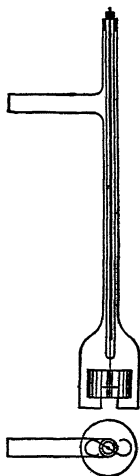


Fig. 33. — Hydrogen electrode.



TABLE III

ELECTRODE POTENTIALS \*

Electrode Reactions	$E_0$ in Volts	Electrode Reactions	$E_0$ in Volts
$\text{Li} = \text{Li}^+ + \theta$	2.957	$2\text{Ag} + \text{CO}_3 = \text{Ag}_2\text{CO}_3 + 2\theta$	-0.50
$\text{K} = \text{K}^+ + \theta$	2.922	$\text{Cu} \rightarrow \text{Cu}^+ + \theta$	-0.52
$\text{Ca} = \text{Ca}^{++} + 2\theta$	2.85	$\text{I}^- = \frac{1}{2}\text{I}_2 + \theta$	-0.535
$\text{Na} = \text{Na}^+ + \theta$	2.712	$3\text{I}^- = \text{I}_3^- + 2\theta$	-0.54
$\text{Mg} = \text{Mg}^{++} + 2\theta$	2.3	$\text{Hg} + \text{SO}_4^{--} = \text{HgSO}_4 + 2\theta$	-0.0621
$\text{Zn} = \text{Zn}^{++} + 2\theta$	0.758	$\text{MnO}_4^{--} = \text{MnO}_2 + \theta$	-0.60
$\text{Ag}^+ + 2\text{CN}^- = \text{Ag}(\text{CN})_2^- + \theta$	0.5	$\text{Ag} + \text{BrO}_3^- = \text{AgBrO}_3 + \theta$	-0.68
$\text{Fe} = \text{Fe}^{++} + 2\theta$	0.44	$\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^{--} + 2\text{H}_2\text{O} + 2\theta$	-0.71
$\text{Cd} = \text{Cd}^{++} + 2\theta$	0.397	$\text{Fe}^{++} = \text{Fe}^{+++} + \theta$	-0.74
$\text{Tl} = \text{Tl}^+ + \theta$	0.336	$2\text{Hg} = \text{Hg}_2^{++} + 2\theta$	-0.798
$\text{Ni} = \text{Ni}^{++} + 2\theta$	0.22	$\text{Ag} = \text{Ag}^+ + \theta$	-0.799
$\text{Ag} + \text{I}^- = \text{AgI} + \theta$	0.15	$\text{CuI} = \text{Cu}^{++} + \text{I}^- + \theta$	-0.85
$\text{Sn} = \text{Sn}^{++} + 2\theta$	0.136	$\text{Hg} = \text{Hg}^{++} + 2\theta$	-0.86
$\text{Pb} = \text{Pb}^{++} + 2\theta$	0.122	$\text{NO} + 2\text{H}_2\text{O} = \text{NO}_3^- + 4\text{H}^+ + 3\theta$	-0.95
$2\text{Hg} + 2\text{I}^- = \text{Hg}_2\text{I}_2 + 2\theta$	0.04	$\text{Br}^- = \frac{1}{2}\text{Br}_2 + \theta$	-1.065
$2\text{Ag} + \text{H}_2\text{S} = \text{Ag}_2\text{S} + 2\text{H}^+ + 2\theta$	0.036	$\frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O} = \text{IO}_3^- + 6\text{H}^+ + 5\theta$	-1.19
$\frac{1}{2}\text{H}_2 = \text{H}^+ + \theta$	0.000	$\text{Ti}^+ = \text{Ti}^{+++} + 2\theta$	-1.2
$2\text{Hg} + 2\text{Br}^- = \text{Hg}_2\text{Br}_2 + 2\theta$	-0.13	$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\theta$	-1.23
$\text{Sn}^{++} = \text{Sn}^{+++} + 2\theta$	-0.13	$\text{Mn}^{++} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2\theta$	-1.33
$\text{Cu}^+ = \text{Cu}^{++} + \theta$	-0.17	$\text{Cl} = \frac{1}{2}\text{Cl}_2 + \theta$	-1.359
$\text{Ag} + \text{Cl}^- = \text{AgCl} + \theta$	-0.223	$\text{Au} = \text{Au}^{+++} + 3\theta$	-1.36
$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2 + 2\theta$	-0.27	$\text{Pb}^{++} + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{H}^+ + 2\theta$	-1.44
$\text{Cu} = \text{Cu}^{++} + 2\theta$	-0.344	$\text{Mn}^{++} + 4\text{H}_2\text{O} = \text{MnO}_4^- + 8\text{H}^+ + 4\theta$	-1.483
$2\text{OH}^- = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\theta$	-0.398	$\text{Au} = \text{Au}^+ + \theta$	-1.50
$\text{Fe}(\text{CN})_6^{--} = \text{Fe}(\text{CN})_6^{---} + \theta$	-0.489	$\text{MnO}_2 + 2\text{H}_2\text{O} = \text{MnO}_4^- + 4\text{H}^+ + 3\theta$	-1.586
$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} = \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\theta$	-0.49	$\text{PbSO}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{--} + 2\theta$	-1.70
		$\text{F} = \frac{1}{2}\text{F}_2 + \theta$	-2.8

\* Based for the most part upon the Summary of Electrode Potentials, by Gerkse, Chemical Reviews, 1, 377 (1925).

the same as those at which the electrode potentials were determined. The standard conditions adopted for such determinations are: a temperature of 25° C.; unit activity or approximately molal concentration of the substances in solution, except when these are kept constant by the presence of a slightly soluble solid; unit fugacity or approximately one atmosphere pressure of all gaseous reagents. Further, since the concentration of water in the dilute solutions commonly used does not differ appreciably from that of pure water its activity may be represented by one.

**Change of Potential with Concentration and with Pressure.**

Since the free energy of a process varies in the same manner as its equilibrium constant, it should be possible to predict from the form of the expression for the equilibrium constant of an electrode process how the potential difference is affected by varying concentration and pressure. The value of the electrode potential should be increased by increasing the concentration of the substances used up and decreased by increasing the concentrations of the substances formed by the reaction. This change can be calculated quantitatively by the use of an expression first developed by Nernst, namely

$$E = E_0 - \frac{0.059}{N} \log X,$$

in which  $E$  is the electrode potential at the assumed conditions,  $E_0$  is the potential at standard conditions,  $N$  is the number of electrons concerned in the process, and  $X$  is the expression representing the equilibrium constant for the process when taking place in the assumed direction. Hence the value of  $E$  for the decomposition of water, when  $(H^+) = 0.1$  and the pressure of oxygen gas is one-fifth of an atmosphere, becomes

$$E = -1.23 - \frac{0.059}{2} \log \frac{(.1)^2(.2)^{\frac{1}{2}}}{1} \quad \text{or} \quad -1.161 \text{ volt.}$$

Similarly the value of  $E$  for the precipitation of copper from a solution in which  $(Cu^{++})$  is .1 becomes

$$E = .344 - \frac{0.059}{2} \log \frac{1}{.1} \quad \text{or} \quad .3145 \text{ volt.}$$

Hence the theoretically required voltage needed for the formation of Cu and  $O_2$  from a solution which is 0.1 molal as to both  $Cu^{++}$  and  $H^+$  is 0.8465 volt.

**Polarization and Voltage.** As already noted, electrode potentials are measured with a negligibly small current flowing through the cell. Under such conditions the fall of potential through the cell due to ohmic resistance, since it depends upon the product of the resistance and current strength, approaches zero. In an actual electrolysis, however, a large current must be made use of if the process is to take place in a finite period of time, and under such circumstances the ohmic resistance becomes an important item. This resistance is furthermore a difficult item to estimate since it depends upon a number of factors, especially the conductance and therefore the composition of the solution, the form and size of the two electrodes, the space between them, and the temperature.

It is further assumed that the reactions to which the standard electrode potentials correspond are reversible and rapid. In actual electrolytic processes however this is rarely true, and the discrepancies between actual and theoretical values due to this cause are often large. The voltage also varies with the nature of the metal, and the character of the surface of the electrode. Furthermore, in determining standard electrode potentials a long time period can be allowed to elapse for the attainment of equilibrium, but in an actual electrolytic process this is not possible. Since many electrode processes have very slow rates, large discrepancies may arise between the minimum voltage needed, which is calculated from standard potentials, and those actually needed to cause the process to take place at a reasonable speed. This difference is known as "overvoltage"; its magnitude depends upon many factors, of which the following are the most important. First, there is to be considered the nature of the substance produced by the process. Gaseous substances invariably give much larger overvoltages than solids, and the base metals such as iron and zinc show larger overvoltages than the noble metals like platinum and gold. The second factor is the nature of the electrode surface, both as to its chemical and physical character, especially the smoothness or roughness of the surface. The third

factor involves the "current density," that is, the number of amperes flowing through the circuit per square centimeter of electrode surface. This effect is due to the fact that the solution in the neighborhood of the electrode becomes rapidly depleted of the ion which enters the reaction, or there is an accumulation of the ion formed at the electrode. Unless the solution is made to circulate rapidly some time is required for the process of diffusion to restore the concentration of this particular ion to its original value. Some idea of the magnitude of these effects may be gained by a study of the following table.<sup>1</sup>

I. Overvoltage of metals deposited from an acid solution.

Current density in amperes per sq. cm.	Cu on Cu	Fe on Fe
0.00006	.....	0.108 volt
0.00011	0.011 volt	0.129 volt
0.00227	0.013 volt	0.141 volt

II. Overvoltage of hydrogen from an acid solution.

Current density in ampere per sq. cm.....	0.00005	0.01	0.1
Electrode of smooth platinum.....	.08	.07	.29 volts
Electrode of platinized platinum.....	0.00	.03	.04 volts
Electrode of gold.....	0.02	0.39	.59
Electrode of mercury.....	0.57	1.04	1.07
Electrode of copper.....	0.19	0.58	0.85
Electrode of tin.....	0.40	1.08	1.22
Electrode of iron.....	0.17	0.56	0.82
Electrode of zinc.....	0.48	0.75	1.06

III. Overvoltage of oxygen from an acid solution.

Current density in amperes per sq. cm.....	0.023
Electrode of smooth platinum.....	0.37 -0.42 volt

**Voltage Needed for Complete Precipitation.** The minimum voltage required for complete precipitation of a metal depends upon the composition of the solution at the end rather than at the beginning of the process. If, for example, it is desired to

<sup>1</sup> A summary of data relating to overvoltage is to be found in "The Principles of Electrochemistry," by Allmand and Ellingham.

determine the copper in a tenth molal solution of cupric sulfate, the concentration of the cupric ion should be reduced from 0.1 to a very small value, which necessitates an increase in the concentration of the hydrogen ion from  $1 \times 10^{-7}$  to .2. The electrode potential at the cathode, assuming that ( $\text{Cu}^{++}$ ) is reduced to  $1 \times 10^{-6}$ , which is small enough to be neglected, can be calculated to be + 0.167. The potential at the anode, assuming ( $\text{H}^+$ ) = 0.2 and  $\text{O}_2$  = .2 atmosphere can be calculated to be - 1.178. A fair estimate of the cathodic overvoltage would be - 0.02, of the anodic - 0.4, and of that required to overcome ohmic resistance - 0.5. The net sum of these items is - 1.931 volts. This value is clearly only a rough estimate; the exact value could not be calculated unless certain additional details were specified. This discussion gives an idea of the factors which enter into the determination of the correct value of the required voltage.

## II. Theory of Electrolytic Separations

**Liberation of Hydrogen During Electrolysis.** The electrolysis of solutions containing more than one electrolyte involves the possibility of more than one reaction at both anode and cathode. In order to predict which of the possible changes at the cathode will actually take place, it is necessary to calculate the sum of the cathode potential and overvoltage, that is the decomposition voltage, separately for all possible cathodic reactions. The largest positive or smallest negative voltage found by these calculations determines which of these reactions takes place most readily and will therefore take place in preference to the others. If, however, the circulation of the substance concerned in the reaction, which is within the sphere of attraction of the cathode, is small as compared with that of one of the other substances which may also react, the latter may also undergo reduction simultaneously. Even if the solution contains a single electrolyte only, hydrogen ions gradually accumulate during electrolysis. In the electrolysis of a tenth-molal solution of cupric sulfate already discussed, the values of the deposition potentials for the separation of copper

and hydrogen at different stages of the electrolysis have been calculated to be as follows:

	(Cu <sup>++</sup> )	(H <sup>+</sup> )	Electrode potential plus overvoltage	
			For copper	For hydrogen
Original solution.....	.1	$1 \times 10^{-7}$	+ 3015	-.483
Copper half precipitated....	.05	0.1	+ .294	-.129
Copper $\frac{4}{5}$ precipitated.....	.02	0.16	+ .281	-.117
Copper almost completely precipitated.....	$1 \times 10^{-6}$	0.20	+ .154	-.117
Copper almost completely precipitated.....	$1 \times 10^{-15}$	0.20	-.111	-.117

It is clear that there must be a stage in the process, namely when (Cu<sup>++</sup>) is about  $1 \times 10^{-15}$ , at which the tendency for precipitation of copper and hydrogen is equal. This concentration is, however, so small as to represent a theoretical rather than an actual value, and long before it is reached deposition of hydrogen would begin to take place. The simultaneous separation of hydrogen affects the quantitative process for the determination of copper in two ways; first, it greatly delays the rate of precipitation, and secondly it may result in the formation of spongy or poorly adherent precipitates. Both of these matters will be considered at greater length in subsequent paragraphs.

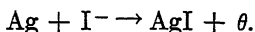
**Separations with Constant Voltage.** The possibility of accurately separating two metals such as silver and copper whose normal electrode potentials are both positive, will depend upon whether the actual values of the deposition potentials required for complete separation of one metal exceeds that necessary for the separation of the other. If the overvoltages of the two are also known, it is easy to calculate with a fair degree of accuracy whether it is probable that such a separation is possible. If the overvoltage of the metal having the smaller electrode potential exceeds that of the other, the possibility of the separation is enhanced, if the reverse is true, it is reduced. If the two over-

voltages are the same, it is easy to see that it would be feasible to separate two univalent metals provided the values for their normal electrode potentials differed by 0.590 volt; or of two divalent metals provided the value for the electrode potentials differed by 0.295 volt. These differences permit of reducing the concentration of one metal to  $1 \times 10^{-10}$  times that of the other. Additional items relating to the rate of separation and purity of the precipitate must however also be considered. Attention should be given to the fact that such separations depend upon the form in which the two metals are present in the solutions. The calculations given assume that all the metal present exists in the form of simple ions only, but it is sometimes possible to greatly alter the relative concentrations of the two simple metallic ions by the addition of other reagents which yield complex ions with one or both of the metals. Separations of this type all depend upon the maintenance of a particular value for the potential difference between the two electrodes. They are sometimes called constant voltage separations.

**Separation with Constant Current.** Separations at a constant voltage assume that sufficient hydroxyl ion is present to keep the concentration of hydrogen ion very small and prevent the separation of hydrogen gas. If hydrogen ion is already present, or if it is permitted to accumulate in the solution, the separation of hydrogen gas rather than a second metal must be considered. In general the presence of even small concentrations of hydrogen ion will make it possible to separate all metals having positive electrode potentials from those having negative electrode potentials. The exact requirement for the separation is that the value of  $(H^+)$  at the outset is such that the deposition potential for hydrogen in the solution is less than that for the more positive of the two metals. It is possible to make such separations with but little regard for potential differences, and since the amperage changes but slightly during the process, such separations are often spoken of as constant current separations. One feature which it is sometimes difficult to avoid is the formation of 'spongy deposits.

**Separations Involving Oxidation.** The table of electrode potentials contains a number of values for processes in which an anion

is oxidized to form an insoluble compound with the metal of which the anode is composed. An example is



Such processes may be made the bases of quantitative processes provided the precipitate can be made to adhere to the electrode without crumbling off while it is being washed, dried and weighed. Unfortunately this is frequently not possible.

Still other oxidation processes depend upon the formation of oxides which can be made to adhere to a platinum anode. They include especially the oxidation of lead ion to  $\text{PbO}_2$  and manganous ion to  $\text{MnO}_2$ . Obviously it should be possible to separate those metallic ions which are easily reduced to metals from those which are easily oxidized to insoluble oxides, either simultaneously or consecutively.

### III. Factors Affecting the Rate of Precipitation

**The Law of Faraday.** The Law of Faraday requires that the amount of chemical change effected by the passage of an electric current through a solution for a specified time, be directly proportional to the atomic or molecular weight of the substance changed and inversely to the number of electrons concerned in the change. The separation of one gram equivalent of any substance requires the passage of 96,500 coulombs of electricity. Stated differently, a current of one ampere would yield 0.00062 equivalents of the substance formed at both anode and cathode per minute.

If all the current which passes through the solution reaches the cathode by neutralization of positive charges on the cation being deposited, the time required for complete precipitation of a known weight can be easily calculated from the amperage. As noted on page 164 it is not possible to carry out a process involving complete precipitation in this manner. Those conditions which insure maintenance of the maximum possible concentration around the cathode, of the cation being precipitated, favor separation of this rather than other ions. However it is impossible to ascertain the actual time required for a precipitation except



by making an actual test under specified conditions. The manner in which the required time is affected by variations in the important factors will be shown by actual experimental data.<sup>1</sup>

**Forms of Electrodes Used.** Electrodes of platinum are to be preferred to those of any of the less noble metals since they can be ignited directly in the flame without change in weight, are not attacked by solutions of acids or alkalis during electrolysis, and can be treated for the removal of the precipitated metal or oxide after electrolysis with strong acids. Owing to the cost of the metal they are made as light as possible in proportion to the available surface. Some of the types of electrodes in general use are here described.

The Classen dish, represented in Fig. 34, serves to contain the solution being electrolyzed and is itself the cathode. The anode used with it is a disk of foil or a horizontally coiled spiral of wire. The size in general use has a capacity of 220 cc. and weighs about 37 grams. This arrangement is very unfavorable for circulation of the solution; furthermore, the removal of the solution and the washing of the deposit are not easily carried out. Its chief advantage is that certain deposits which are but poorly adherent are more easily retained by it without loss than by the other forms of electrodes.

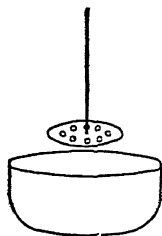


Fig. 34.—Classen dish and anode.

The Mansfield electrodes represented in Fig. 35 consist of a cylindrical cathode of thin foil soldered to a supporting wire and an anode of a cylindrically coiled spiral of wire which is placed inside the cylinder. This device gives fairly good stirring of that portion of the solution inside the cathode owing to the currents produced by oxygen liberated at the anode, but these currents affect the annular space outside the cathode only slightly. In an actual experiment in which a known amount of copper was completely precipitated on an electrode of this form, it was found that 90 per cent of the metal was precipitated on the inner surface of the cathode, clearly indicating that the efficiency of the

<sup>1</sup> Jour. Am. Chem. Soc. 32, 1264 (1910).

outer cathode surface was very small owing to the poor circulation of the ions in this portion of the solution. Its efficiency was greatly increased by drilling many small holes in the cathode.

The Winkler cathode shown in Fig. 36 consists of a cylinder of fine gauze supported by a wire of small size. The form represented is 3 cm. in diameter and 6 cm. in length; the gauze is composed of wire .06 mm. in diameter with 41 meshes per linear centimeter. Unlike the Mansfield form it offers practically no

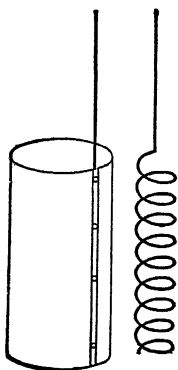


Fig. 35.—Mansfield electrodes.

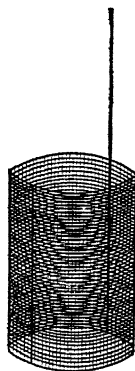


Fig. 36.—Winkler cathode.

barrier to the circulation of the solution and therefore the deposition is much more rapid, and there is much less danger of obtaining spongy deposits.

Another type of cathode consists of a small amount of mercury in the bottom of a beaker or flask containing the solution of the metal to be deposited, contact between the mercury and the battery being made by means of a platinum wire sealed into the bottom of the beaker. It is especially advantageous in precipitating metals which give poor deposits or those, such as sodium, whose normal electrode potentials are large. Since the separated metal dissolves in the mercury the potential actually needed represents the difference between the ion of the metal in the aqueous solution and the metal in the mercury, and may be made much less than that of the normal potential for that metal. The disadvantages of this type of electrode are its comparatively

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large weight and the need of great care in washing and drying before weighing.

The comparative efficiencies of the first three electrodes described are shown in the following table, which gives the approximate weights, available surfaces, and the length of time needed for the precipitation of 0.1975 gram of copper under identical conditions.

Cathode used	Surface exposed, sq. cm.	Weight of cathode, grams	Time required, minutes
Classen dish.....	100	37	400
Mansfield cathode.....	79	11	450
Mansfield, with holes.....	78	11	390
Winkler cathode.....	93	4.2	50

**Change of Current.** As already noted the rate of deposition is in accord with the requirements of Faraday's Law only so long as the concentration of the metallic ion is so great that a sufficient number of ions are within the sphere of attraction of the cathode to take up the electrons as rapidly as they are supplied to the cathode. Increasing the current strength has two effects. First, it increases the rate at which electrons are supplied, and second, it increases the circulation of the solution by increasing the volume of oxygen gas liberated at the anode. The latter effect greatly increases the time over which the precipitation is in accord with Faraday's Law. The actual net effect of varying current depends upon a large number of factors. It can be illustrated by means of the graph shown in Fig. 37, representing the results of five experiments in each of which 0.1975 gram of copper, as copper sulfate, was precipitated from a solution containing 2 grams of ammonium nitrate, 4 cc. of concentrated nitric acid, and a total volume of 140 cc. Winkler gauze electrodes were used and a current strength of 0.19, 0.34, 0.5, 0.78, and 5.5 amperes, respectively, were maintained continuously throughout the different experiments. These curves clearly show that the time interval during which the precipitation is directly proportional

to the time is greatly increased by increasing amperage, clearly demonstrating the importance of circulation of the solution.

**Change of Concentration.** The volume of the solution from which the metal is precipitated is of importance only in the effect it has upon the concentration of the metallic ion in the solution, and the circulation of the solution caused by the liberated oxygen gas. Obviously it is desirable to keep the total volume as

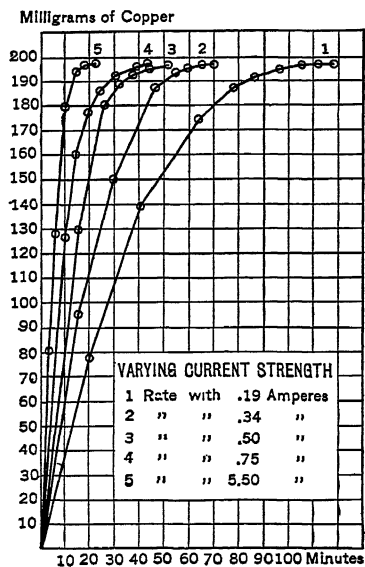


Fig. 37.—Curves showing rate at which copper is precipitated.

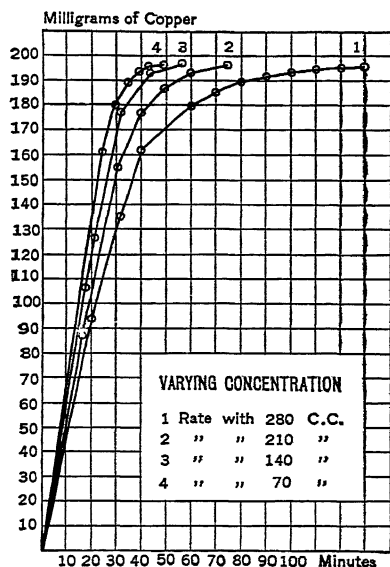


Fig. 38.—Curves showing rate at which copper is precipitated.

small as possible, since this insures both a larger concentration and a more effective circulation. The actual effect of varying concentration on the rate of precipitation is shown by the graphs of Fig. 38. These graphs represent a series of experiments in which 0.1975 gram of copper as copper sulfate was precipitated from solutions diluted to 70, 140, 210 and 280 cc. respectively. The solution also contained 1 cc. of concentrated nitric acid and 2 cc. of concentrated sulfuric acid for each 140 cc. A Winkler gauze cathode and a current of 0.311 ampere were used in all

these experiments. These curves confirm the statements already made.

#### IV. Factors Affecting the Character of Deposits

**Necessary Requirements.** The weight of substance precipitated by the action of the current is usually ascertained by determining the increase in the weight of the electrode at which precipitation takes place. This necessitates the substitution of pure water or some other pure and easily volatile liquid, for the solution in contact with the electrode, and elimination of the volatile liquid by evaporation. These operations may result in large mechanical losses of the precipitate unless it possesses the proper texture and is firmly adherent. Deposits which are spongy, and therefore easily detached, or coarsely crystalline and therefore brittle or crumbly, or pulverulent and therefore having little coherence, cannot be used with success. The adherence of the deposit depends to some extent upon the nature of the electrode surface. A slightly roughened surface has been found to be somewhat more favorable than a smooth surface, but by far the most important effects are concerned with the conditions under which the precipitate separates.

**Effect of Varying Rate of Precipitation.** Experience shows that the character of an electrolytic deposit depends primarily upon the ratio of electrode surface on which the deposition takes place to the rate of deposition. Apparently a certain minimum amount of space must be allotted to each anion or cation discharged in order that the resulting molecules may adjust themselves to the surface and build up a stable structure. The limiting current density which can be safely used is greatly increased by the use of gauze electrodes rather than those of foil. This has been attributed to the favorable effect of curved as compared with plane surfaces, but it is probably the result of better stirring of the solution. The conditions necessary to yield a satisfactory deposit must be ascertained by actual experiment for every substance. In general, it is easier to obtain satisfactory deposits of metals than of insoluble oxides or salts, such as sulfides and iodides, and with noble than with base metals.

**Effect of Associated Electrolytes.** As already noted, hydrogen gas frequently separates along with the cathode deposit. If the proportion of hydrogen to metal is large, the latter may be spongy, owing to entangled gas and so loosely adherent as to make an accurate determination impossible. The proportion of hydrogen in the deposit may be reduced by decreasing the concentration of hydrogen ion in the solution or by reducing the current used. Another remedy is to introduce nitrate ion, which is supposed to prevent liberation of hydrogen gas through its oxidizing power. It is easily shown that copper deposited from a solution containing nitrate and hydrogen ion is much smoother and more adherent than that obtained from a solution containing sulfate and hydrogen ion. The presence of even small concentrations of chloride ion yields poor precipitates. This has been attributed to the separation of insoluble cuprous chloride with the metal.

**Deposition from Solutions of Complex Ions.** The impossibility of obtaining complete separation of certain metals and of getting satisfactory deposits of others, when separated from solutions of simple salts, has led to the use of certain reagents which form complex ions with these metals. Thus by the addition of ammonium sulfide to a solution of a salt of antimony,  $\text{SbS}_3^{---}$  is formed, and when added to a solution of a tin salt,  $\text{SnS}_3^{--}$  is formed. Similarly, by adding a soluble cyanide to a solution of a silver salt,  $\text{Ag}^-(\text{CN})_2$  is formed. The complex constant, that is, the equilibrium constant for the formation of these complexes from the simple ions, is in every case large, and the concentration of the simple ion left in the solution extremely small. Precipitation from such solutions probably involves separation of the simple ion only, but is associated with conversion of complex into simple ions as the concentration of the latter is reduced. Apparently the rate of conversion of complex into simple ions is usually large, but it is clear that the electrode potentials needed for such depositions are very different from those needed for separation from solutions of simple salts. The effect on the overvoltage value is also large and therefore the decomposition potentials of the same metal in the two classes of solutions may vary greatly.

The addition of such reagents as those named greatly improves the character of the deposits. None of the metals cited can be

separated in a form suitable for weighing except in the presence of such reagents. An additional effect of these reagents is to make it possible to keep certain metals in solution even if the latter is slightly basic, which reduces to a minimum the separation of hydrogen during electrolysis and makes possible the separation of certain metals which are much more positive than hydrogen.

**Contamination of Deposits.** A number of secondary reactions may lead to the contamination of the separated deposit with small amounts of other substances. Certain metals, such as iron, nickel, and cobalt, when separated under such conditions as to result in the simultaneous separation of hydrogen, take up and retain appreciable amounts of the latter, probably as hydrides. This affects the nature of the cathode, and therefore both the electrode potential and the overvoltage at the cathode, and the physical properties of the deposit as well as its actual weight. Again, if iron is deposited from solutions containing certain of the reagents used to form complex ions, especially soluble citrates, the deposit is found to be contaminated with appreciable amounts of carbon. Changes in the basicity of the solution during electrolysis may result in the separation of appreciable amounts of insoluble hydroxides at the cathode. Still another effect may result from the presence of the halide ions. The decomposition voltage of iodide, bromide, and even of chloride ion, is sufficiently low to permit the separation of the free halogens at the anode, which by their action on the platinum anode yield platinum ions, which are in turn reduced at the cathode, increasing the weight of the deposit.

## V. Apparatus Required for Electrolytic Precipitations

**Set-up for a Single Determination.** The current required for an electrolytic process must be furnished at a voltage which exceeds the decomposition voltage of the electrolyte plus that needed to overcome the external resistance and which yields a current of sufficient strength to complete the precipitation within a reasonable time period. It is further desirable that the voltage available be much greater than that actually needed, for, by

introducing a variable resistance or rheostat in the circuit, a wider range of current strengths is available. These conditions are best satisfied by using a storage battery or a series of galvanic cells which can be depended upon to yield an approximately constant voltage for a long period of time. Two storage cells of the usual lead — lead dioxide type, which yield about 4.4 volts, or four Daniell cells, suffice for the usual range of determinations made. In order to insure maintenance of the proper conditions during electrolysis an ammeter should be introduced into the main circuit to show the current, and a voltmeter should be intro-

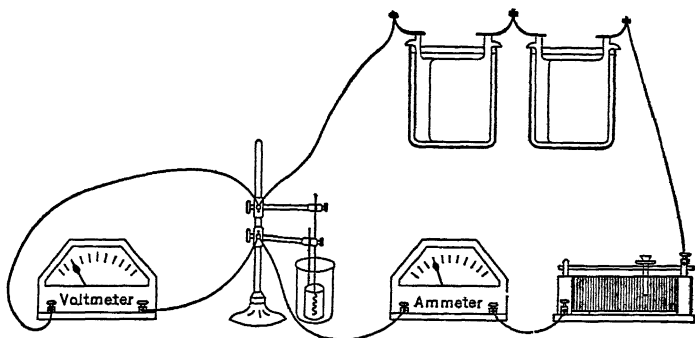


Fig. 39.—Apparatus for a single electrolytic determination.

duced into a shunt circuit connecting the two electrodes to show the potential difference between them. A special form of stand is needed to support the anode and cathode, and to provide a simple method of connecting the former with the positive and the latter with the negative pole of the battery. Short circuiting of the current through the stand is avoided by using a glass rod as the support for the two arms to which the electrodes are clamped. The proper arrangement of the different parts of the set-up is shown in Fig. 39.

**Set-up for a Series of Determinations.** Although several solutions may be electrolyzed in the same circuit if a sufficiently large voltage is used, the same current necessarily passes through all, and if several different metals are being precipitated it may not be possible to satisfy the conditions for each determination.



Furthermore, after precipitation in any of the solutions has been completed, the current must be interrupted while the electrodes are being removed, possibly permitting some of the precipitate in the other solutions to redissolve. For these reasons it is necessary to split up the main current into as many shunt circuits as there are determinations to be made. If all the solutions represent the same decomposition potential and offer the same resistance, the current passing through each shunt circuit would be the same and could be easily regulated by varying the number of battery cells used, or by introducing resistance in the main circuit. If the different solutions represent different decomposition voltages and offer different resistances, the current flowing through each shunt circuit must be regulated by a separate resistance. By using the proper switches and making the necessary connections, the same set of measuring instruments may be used for the entire series of shunt circuits. Such an arrangement is represented on page 201, showing two out of any desired number of shunt circuits, each of which is provided with a separate rheostat. This shows the connections by which either of two ammeters or a voltmeter may be thrown in or out of the circuit. One of these ammeters is used for the measurement of currents exceeding an entire ampere, the other for fractions of an ampere. The wires used for the connections are of copper and are so large that their resistance is negligibly small.

**The Use of Mechanical Stirring Devices.** Circulation of the solution during deposition may also be effected by mechanical stirring. The device usually employed consists of a small paddle-wheel, or a loop of wire, which is placed near the center of the beaker containing the solution, and is driven by a small electric motor. The stirrer may be made of platinum and used as anode or cathode, or may be of glass and form no part of the electric circuit. The chief gain resulting from such devices is that high current densities, which would give poor deposits in solutions less effectively stirred, can thus be used. A secondary effect resulting from the use of large currents is the rapid heating of the solution. In some determinations this is not objectionable, but where metals are being deposited from acid solutions much larger errors may result from re-solution of the precipitated metal while the

electrodes are being detached and washed. Complete precipitation of the amounts of metal usually employed for these determinations can be made within an hour without use of mechanical stirring, if the volume of the solution is kept small and if gauze electrodes of the proper form, properly placed in the solution, are used.

### Questions and Problems. Series 10

1. Explain why, in the electrolysis of a solution of cupric sulfate between copper electrodes, cupric ion rather than oxygen gas is found at the anode.

2. What combination of electrode reactions would require the largest possible potential difference? What combination would yield the smallest possible potential difference?

3. Write the proper electrode reactions for the electrolysis of (a) a tenth-molal solution of ferric sulfate between iron electrodes, (b) a molal solution of hydrochloric acid between silver electrodes, (c) a molal solution of sodium iodide between platinum electrodes, (d) a solution of potassium hydroxide containing precipitated manganese dioxide between platinum electrodes.

4. A solution in which the concentrations of cupric ion and silver ion are both tenth molal is electrolyzed between platinum electrodes. At what concentration of silver ion will copper begin to deposit? *Ans.*  $6.2 \times 10^{-3}$ .

5. Assuming that it is justifiable to add and subtract free energy equations, show that the value of the electrode potential for  $\text{Fe} \rightarrow \text{Fe}^{+++}$ , is in agreement with the values for  $\text{Fe} \rightarrow \text{Fe}^{++}$  and  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$ .

6. Assuming that a solution containing a molal concentration of sodium ion is electrolyzed, using a mercury cathode, what would be the cathode potential difference when the concentration of sodium in the mercury of the cathode is .001 mole per liter? *Ans.* — 2.535 volts.

7. A potential difference of two volts is established between two platinum electrodes in a solution containing 0.1 molal concentrations of  $\text{Sn}(\text{SO}_4)_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ , and  $\text{H}_2\text{SO}_4$ . Give the successive reactions at the cathode and explain the principle upon which your answer is based.

8. Calculate the electromotive force of a cell in which molal concentrations of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{Br}_2$  are the active reagents. Calculate the free energy of the reaction and show how it would change by dilution the mixture to twice the original volume.

9. Outline a procedure for the determination of nickel and copper in an alloy containing about 70 per cent of nickel, 25 of copper and small amounts of iron and manganese.

## CHAPTER XIV

### DETERMINATION OF CHLORINE IN A SOLUBLE CHLORIDE

#### I. Facts upon Which the Determination is Based

**Properties of Silver Chloride.** When first precipitated, silver chloride is so finely divided that it is difficult to separate from the solution with an ordinary filter. However if the solution is slightly acid, and if kept hot and stirred vigorously, or if allowed to stand for several hours, the fine particles gradually coalesce, and, owing to their high density, rapidly settle to the bottom of the containing vessel. Since the silver nitrate solution used for this determination is not employed for other precipitations, it is convenient to make it of such strength that 1 cc. will react with an amount of chloride ion represented by a whole number of milligrams. A solution made by dissolving 24 grams of the pure silver nitrate in 1 liter of water, 1 cc. of which equals approximately 0.005 gram of chlorine, is a desirable one to use.

The solubility of silver chloride is extremely small; it is increased by the presence of large concentrations of nitric or hydrochloric acids, and the chlorides and nitrates of ammonium and the alkali metals. When digested with pure water it slowly changes into a colloidal form, but this change is prevented by the presence of a small amount of nitric acid or of any other soluble electrolyte.

When freshly precipitated silver chloride is exposed to strong sunlight, it darkens and chlorine is liberated; the change is probably due to the formation of a sub-chloride, to which the formula  $\text{Ag}_2\text{Cl}$  has been assigned. Since the precipitate is not transparent the action is purely superficial, and the percentage acted upon is small unless the mass of precipitate is continually broken up by stirring.

Pure silver chloride fuses at  $455^\circ\text{C}$ . without change of compo-

sition, and produces a yellow viscous liquid which forms a tough horny mass when allowed to solidify. It begins to be appreciably volatile at about the same temperature and appreciable amounts may be sublimed if kept at this temperature for ten minutes.

Like most of the compounds of silver this precipitate is easily reduced to the metal by even weak reducing agents. The efficiency of organic matter as a reducing agent makes it necessary to use extreme care in igniting the precipitate when separated on a filter paper, and renders the use of an asbestos filter preferable.

**Possible Errors from Associated Salts.** Since silver chloride is always precipitated from solutions which have been made acid by the addition of nitric acid the possibility of error resulting from the separation of silver oxide, carbonate, cyanide, borate, phosphate, or arsenate, or from the solvent action of ammonium hydroxide or potassium cyanide, is eliminated. The presence of sulfides or thiosulfates may necessitate evaporation with an excess of acid to eliminate hydrogen sulfide or sulfur dioxide, and in the latter case removal by filtration of precipitated sulfur. The only objectionable substances which are likely to be present in usual salt mixtures are bromides, iodides, and sulfocyanates. It is assumed that the sample, the analysis of which is outlined below, does not contain these ions, and only small amounts of sulfates, carbonates, borates, and phosphates.

## II. Outline of the Method of Procedure

**Preparation of Solution, and Precipitation.** Place 1 or more grams of the sample in a small weighing tube, and weigh accurately. Hold the tube over a clean 300-cc. beaker, remove the stopper and carefully pour into the beaker from 0.2 to 0.4 gram of sample, then replace the stopper and again weigh accurately. Add to the sample 50 cc. of water, and then introduce 6 N nitric acid, a few drops at a time until the solution is distinctly acidic, and then add 1 cc. in excess. This should be determined by placing a stirring rod which is moistened with the solution on a piece of blue litmus paper and noting the color. After completing the test, rinse off the paper into the beaker with a few cubic centimeters of distilled water. If the acid causes effer-

vescence it is well to warm slightly to eliminate the dissolved gas. If an insoluble residue remains, filter through a small filter into a clean beaker and wash, being careful to wash the entire filter, not the apex only. Dilute, if necessary, to bring the volume up to 100 cc.

Calculate the volume of reagent silver nitrate solution needed to precipitate all the chlorine, assuming that the sample contains as much chlorine as pure sodium chloride. Add slowly, and with constant stirring, 5 cc. in excess of the calculated amount of silver nitrate solution, heat slowly almost to boiling, and keep at or near this temperature with occasional stirring until the precipitate coagulates and the supernatant liquid is clear: or, allow the beaker to stand for several hours. The beaker should be kept away from direct sunlight as much as possible.

**Separation and Ignition of the Precipitate.** Connect a clean Gooch crucible with a suction flask as shown in Fig. 30. Attach the flask to the suction pump and add sufficient asbestos pulp to leave a compact layer about 2 mm. thick, when drawn against the bottom of the crucible by means of the pump, and then place a thin Witt filter plate on top of the asbestos. Pass at least 100 cc. of distilled water through the filter in order to remove all loosely adhering fibers from the outside of the filter and wash out any hydrochloric acid used in preparing the asbestos pulp. Remove the crucible from the filter tube, place in a nickel muffle, and heat for about twenty minutes to a temperature of  $200^{\circ}\text{C}$ . Cool in a desiccator and then weigh accurately.

Clean and rinse the suction flask, connect the crucible with it as before, start the pump, and decant the solution from the silver precipitate through the crucible. Add to the precipitate in the beaker about 25 cc. of water, stir the mixture for a few minutes, then allow it to settle and again decant through the filter. Wash with three more 25-cc. portions of water, to each of which about half of 1 cc. of dilute nitric acid has been added. Transfer the precipitate from the beaker to the filter by means of a stream from the wash bottle, directed back of the precipitate. Finally loosen all particles of precipitate which adhere to the surface of the beaker by means of a rubber-tipped rod and rinse these also into the filter. Empty the filter flask into a clean beaker and

ascertain whether an excess of silver ion is present by the addition of a few drops of dilute silver nitrate solution. Rinse out the filter flask, connect with the filter, pass another 25 cc. of water acidified with nitric acid through it, and test this for silver ion by means of a drop of hydrochloric acid solution. If this shows an appreciable turbidity, continue washing with water containing acid until a further test shows that the silver salt has been removed from the precipitate. Finally wash with 10 cc. of pure water.

Place the crucible in a muffle, heat slowly to  $200^{\circ}\text{C}$ ., keep at that temperature for twenty minutes, then allow to cool, and weigh accurately. Again heat for ten minutes and weigh again, and continue heating and weighing until consecutive weighings do not differ by more than 0.3 mg. Calculate and report the percentage of chlorine present.

**Further Details.** This is an ideal precipitation process. The very slight solubility of the precipitate, its very slight ability to occlude other substances, and the ease with which as much as 2 or 3 grams can be transferred to a filter, washed free from soluble salts, and dried, make it possible to reduce the error of the determination to a very small figure. The actual error, where the ordinary precautions are taken, should be less than one part in five hundred.

### Questions and Problems. Series 11

1. Calculate the chemical factor which should be used in converting a known weight of silver chloride obtained in an analysis into the weight of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  which the sample must have contained. *Ans.* 0.8522.

2. Give the series of reactions showing how metallic silver is produced when (a) silver sulfate is ignited, (b) when silver chloride is fused with sodium carbonate, (c) silver chloride associated with filter paper is heated in a crucible.

3. Chlorine is determined by weighing out 0.25 gram of a sample containing 60.12 per cent of this element dissolving in water and a little nitric acid and adding 35.4 cc. of silver nitrate solution, 1 cc. of which is equivalent to 0.005 gram of chloride ion. What weight of silver chloride remains dissolved in the filtrate assuming that its total volume is 200 cc.? What departure from the correct result would this cause? *Ans.*  $8.3 \times 10^{-7}$  and 0.00008 per cent.

4. If so much of a silver chloride precipitate was reduced that one-fourth of the precipitate actually weighed consisted of  $\text{Ag}_2\text{Cl}$ , how large a departure from the correct percentage is 60.12? *Ans.* 2.1 per cent.

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5. A certain mixture consists of 0.1 gram of sodium chloride, and one of sodium acetate and 200 cc. of water. What weight of silver nitrate could be added to the mixture before silver acetate would begin to separate, assuming that the solubility product of silver acetate is  $3.48 \times 10^{-3}$ ?

*Ans.* 2.229 grams.

6. A mixture is made by dissolving two-tenths of a gram of sodium chloride and one-tenth gram of potassium bromide in 200 cc. of water and then adding 20 cc. of reagent silver nitrate solution. What is the ratio of chloride ion to bromide ion in the resulting solution? Calculate the percentage of silver chloride in the resulting precipitate.

*Ans.* 256 and 64.58 per cent.

7. Suggest a detailed procedure for the determination of chloride ion in seawater assuming that it contains chlorides, sulfates and small amounts of bromides and borates of sodium, potassium and magnesium.

8. A mixture of pure NaCl and NaBr, which weighs 0.5142 gm., yields a precipitate of AgCl plus AgBr which weighs 1.1585 gm. Calculate the percentages of the two components.

*Ans.* 68.31 NaCl and 31.69 NaBr.

9. It is found that when 1.83114 gm. of carefully purified NaCl is converted into AgCl the weight obtained is 4.48983 gm. Calculate the atomic weight of sodium assuming that of chlorine is 35.46 and that of silver is 107.88.

10. In determining NaCl in a series of samples it is desired to use such weights of sample that the weights of AgCl found, when expressed in grams, multiplied by 100 shall give the correct percentages of NaCl present. What weight of sample should be used?

## CHAPTER XV

### DETERMINATION OF SULFUR IN SOLUBLE SULFATES

#### I. Facts upon Which the Determination is Based

**Properties of Barium Sulfate.** The solubility of barium sulfate at room temperature is 0.0023 gram per liter; it is increased slightly by small concentrations of hydrochloric and nitric acids; it is decreased slightly by very small concentrations of sulfuric acid; but the salt is very readily soluble in concentrated sulfuric acid. Barium sulfate has a density of 4.49 grams per cc. and when precipitated under the proper conditions settles rapidly. As much as 2 grams of the precipitate can be easily and rapidly filtered and washed on a 11-cm. filter.

**Barium Sulfate is a Typical Pulverulent Precipitate.** When made to separate by the addition of a salt of barium to a cold concentrated solution of a soluble sulfate, it is usually so finely divided that it cannot be retained on the filters usually employed. Although long continued digestion may increase the size of the particles of such a precipitate somewhat, it is usually impossible to increase them enough to make filtration possible. The difficulty can be avoided by precipitating from a hot solution whose concentration as to sulfate ion does not exceed 3 grams per liter. The presence of a small amount of hydrogen ion seems to make the precipitate more compact, causes it to settle more rapidly, and reduces its tendency to creep.

The conditions which result in the formation of a precipitate of the most desirable physical properties also result in the formation of supersaturated solutions. Under the conditions which are outlined further on, the precipitate should be allowed to stand for at least an hour before filtration. Increasing the amount of acid seems to increase the time necessary for complete separation.



Pure barium sulfate is not decomposed appreciably by heating in dry air up to  $1400^{\circ}\text{C}$ . If heated in the presence of carbon, carbon monoxide, or other reducing agents, it is partially reduced to the sulfide, even at a temperature of  $600^{\circ}\text{C}$ . The presence of moisture seems to favor the reduction. If the precipitate is separated on a paper filter and ignited with the latter without previous drying, sufficient barium sulfide to cause appreciable errors may be formed. The sulfide can be changed back into the sulfate by moistening with dilute sulfuric acid, evaporating to dryness and again igniting, but extreme care must be taken to avoid mechanical losses during the evaporation. Separation of the precipitate on an asbestos filter has decided advantages, but special care must be taken in making the precipitation and in preparing the filter, or filtration is impossible.

**Possible Errors from Associated Salts.** The precipitate produced by the addition of a salt of barium to a slightly alkaline or even a neutral solution of a soluble sulfate may contain, in addition to barium sulfate, small amounts of basic sulfates, and, as a result of the absorption of carbon dioxide from the air, of barium carbonate. The presence of a slight concentration of hydrogen ion prevents the formation of any of these compounds. However, if the concentration of hydrogen ion is not kept small, low results are obtained owing to the fact that an appreciable amount of an acid sulfate of barium, which loses sulfuric acid when ignited, is occluded. The maximum concentration of hydrogen ion should not greatly exceed .02 mole per liter.

Owing to the remarkable tendency of barium sulfate to occlude a large number of anions and cations as discussed on page 142, a special effort should be made to keep the concentration of all the ions of the solution low. Those ions which are largely occluded should be separated by precipitation or changed into ions which are occluded less, using reagents which add only those ions which are themselves but slightly occluded. The nitrate, nitrite, and chlorate ions, all of which cause high results, can be replaced by chloride ion by evaporation with an excess of hydrochloric acid (see page 39). Ferric ion, which causes low results, can be reduced to ferrous ion by certain metals or by hydroxylamine, or it can be changed to a complex ion by citric or tartaric

acids, or it can be precipitated by hydroxyl ion. The presence of potassium and ammonium ions causes slightly low results even though offset to some extent by the positive error resulting from the presence of an equivalent amount of chloride ion.

It is obvious that the precipitating agent used should be barium chloride rather than barium nitrate. A solution containing 76.3 grams of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per liter, 1 cc. of which is capable of precipitating 0.01 gram of sulfur when present as sulfate ion, is a convenient reagent to use.

**Best Conditions for Precipitation.** The ideal conditions for the separation of barium sulfate cannot be specified for all mixtures with any degree of assurance. The final result is always the net sum of a number of plus and minus errors whose magnitudes are difficult to predict. When the sulfate ion is associated with positive ions which are but slightly occluded, the best conditions for the separation are summarized as follows:

- (1) Use of enough sample to yield from 1 to 2 grams of precipitate—assuming this does not necessitate use of an excessive amount of sample.
- (2) Presence of a slight excess of hydrochloric acid—normally about 1 cc. of 6 N acid for 300 cc. of solution.
- (3) Dilution to 300 cc. and heating to the boiling point before adding precipitating reagent.
- (4) Addition of about 2 cc. of precipitating reagent in excess of the theoretically required amount, the reagent being added slowly and with constant stirring.
- (5) Allowing mixture to stand for an hour before filtering.
- (6) Filtration on a paper filter and separation of precipitate from filter before burning latter, or on a Gooch filter if a thick layer of very finely pulped asbestos is used.

### III. Preliminary Qualitative Experiments

**Illustrating the Effects of Varying the Conditions of Precipitation.** Procure a sufficient amount of a solution of sodium sulfate (25 cc. of a solution containing 24.33 grams per liter) to yield about 1 gram of barium sulfate, add 1 cc. of 6 N hydrochloric acid, dilute to 300 cc., heat almost to boiling, and then add slowly and with constant stirring 2 cc. in excess of the theoretically required amount of barium chloride reagent. Allow the

precipitate to settle for a few minutes, then filter on a 11-cm. filter, and wash twice with 10-cc. portions of water.

Procure a similar amount of sodium sulfate solution, add 8 drops (about one-third of a cubic centimeter) of 6 N hydrochloric acid, dilute to 100 cc., add the same volume of barium chloride reagent and filter and wash as in the preceding experiment. Contrast the precipitates obtained in the two experiments as to (a) appearance, (b) rate of settling, and (c) completeness of the separation. If it is not possible to retain either of the precipitates on the filter try the effect of allowing them to stand in contact with the filtrate for an hour.

**Illustrating the Occlusion of Nitrate Ion.** Procure a sufficient amount of sodium sulfate solution to yield 1 gram of barium sulfate, add sufficient potassium nitrate solution (25 cc. of a solution containing 40 grams per liter) to give 1 gram of potassium nitrate, then 1 cc. of 6 N hydrochloric acid, heat to boiling, and add slowly, with constant stirring, 2 cc. in excess of the theoretically required amount of barium chloride, and allow to stand for an hour. Decant the clear portion of the solution through a 11-cm. filter, then add 25 cc. of water, digest for a few minutes, and then filter. Repeat the washing with two more 25-cc. portions of water, then transfer the precipitate to the filter and continue washing until 25 cc. of the washing do not give a test for chloride ion.

Dry the filter thoroughly (best over the sand bath), then transfer as much precipitate as can be easily separated to a crucible and ignite the latter. Place a few drops of water in the crucible and then add a piece of sensitive red litmus paper. Note any color change and explain the result.

### III. Outline of Method of Procedure

**Preparation of Solution.** It will be assumed that the sample used contains, in addition to sulfates, small amounts of chlorides, carbonates, and bicarbonates of those metals whose cations are not badly occluded, and small amounts of insoluble substances, not however including difficultly soluble sulfates.

Weigh out into a 200-cc. beaker sufficient sample to yield

about 1 gram of barium sulfate, assuming in the absence of more definite information that the sample is pure sodium sulfate. Add 25 cc. of water, a drop of methyl orange indicator, and then 6 N hydrochloric acid drop by drop till the solution acquires a permanent pink color, even after heating almost to boiling, and then add 1 cc. of this acid in excess. If an insoluble residue remains, filter through a 9-cm. filter into a 450-cc. beaker and wash the filter, rim as well as apex, with at least 100 cc. of water. Dilute the filtrate and washings to 300 cc.

**Precipitation.** Heat the solution almost to boiling and add slowly and with constant stirring 2 cc. more of reagent barium chloride than is theoretically required to react with the sulfate ion present. Set the beaker aside for an hour and, while waiting, ignite and weigh accurately a small (about 8 cc.) porcelain crucible.

**Separation of Precipitate.** Fold a 11-cm. filter paper to fit accurately a funnel of somewhat larger size, and filter the solution through it, keeping the precipitate as far as possible in the bottom of the beaker. Add 25 cc. of water, mix thoroughly with the precipitate, allow the mixture to stand for a few minutes, and then pour through the filter. Repeat the washing with two more 25-cc. portions of water. Finally transfer the precipitate to the filter, loosening the precipitate which usually adheres to the bottom and sides of the beaker, by means of a rubber-tipped rod. Continue washing the precipitate on the filter till 25 cc. of the washings do not give a test for chloride ion. Finally rinse most of the precipitate into the apex of the filter with a stream from the wash bottle.

**Ignition of Precipitate.** Place the funnel containing the filter on a metal cone and allow the latter to stand over a hot plate or sand bath till the filter is perfectly dry. Separate the precipitate as far as is easily possible from the filter and complete the ignition as directed on page 154. After the final weighing, add to the precipitate in the crucible two drops of 6 N sulfuric acid and ascertain whether the odor of hydrogen sulfide can be detected. If it is recognized, place the crucible on a hot plate and evaporate the acid cautiously. The temperature must be very carefully regulated to avoid mechanical losses. Finally ignite and again weigh. Calculate and report the percentage of sulfate ion present.

## IV. Further Details Regarding the Method

**Accuracy.** An ideal procedure for this determination cannot be formulated without more definite information as to the composition of the sample used. A more accurate estimate of the best amount of sample to use, and the proper amount of precipitating agent to add, can be made in a second determination. A rough estimate of the probable error from occlusion and other sources can be made if the nature of the cations present is known. The following results indicate the magnitude of the errors, expressed in grams of barium sulfate, found in a series of determinations in which sufficient amounts of the sulfates listed in the first column were used to yield exactly 1 gram of barium sulfate.

ERRORS IN DETERMINATION OF SULFATE ION IN VARIOUS SULFATES

Sulfate Used	Errors in Three Separate Determinations			Average Error
$\text{Na}_2\text{SO}_4$ .....	-0.0018	-0.0020	-0.0020	-0.0020
$\text{K}_2\text{SO}_4$ .....	-0.0058	-0.0067	-0.0053	-0.0059
$(\text{NH}_4)_2\text{SO}_4$ .....	-0.0041	-0.0042	-0.0041	-0.0041
$\text{MgSO}_4$ .....	-0.0019	-0.0009	+0.0005	-0.0011
$\text{ZnSO}_4$ .....	+0.0001	0.000	+0.0005	+0.0002
$\text{CuSO}_4$ .....	-0.0003	-0.0011	+0.0005	-0.0003

## / IV. Questions and Problems. Series 12

- /1. Assuming that the ideal conditions for the determination are those formulated on page 185, what volumes of 6 N hydrochloric acid and barium chloride reagent should be used in precipitating (a) 2 grams of barium sulfate from a 300-cc. solution, (b) 1 gram of barium sulfate from 750 cc. of solution?
- /2. How would you proceed in order to test for occluded (a) barium chloride, (b) sulfuric acid, (c) ammonium sulfate, and (d) barium permanganate, in precipitates of barium sulfate?
- /3. A precipitate of barium sulfate is made to separate from a solution containing nitrate ion; it is "purified" by dissolving in concentrated sulfuric acid and reprecipitating by adding a large amount of water. If this precipitate is separated and weighed will it accurately represent sulfate ion present in the original solution?

4. Write reactions for the reduction of barium sulfate by (a) carbon, (b) carbon monoxide, and (c) hydrogen.

5. A precipitate of pure barium sulfate weighing 1 gram is digested with 250 cc. of a solution containing 5 grams of sodium carbonate. Assuming that the solubility, in grams per liter, of barium carbonate is 0.0178, and of barium sulfate is 0.0023, what weight of barium carbonate should be formed?

(Note.—In solving this problem assume that at equilibrium the ratio of  $(\text{CO}_3^{--})$  to  $(\text{SO}_4^{--})$  equals the ratio between the solubility products of barium carbonate and barium sulfate. If  $x$  is used to represent  $(\text{CO}_3^{--})$  at equilibrium it is possible to formulate an expression in which the  $\text{SO}_4^{--}$  which passes into solution is equated to the  $\text{CaCO}_2$  which precipitates.)

6. From the data given on page 140, what weight of BaO would you expect to be present when 1 gram of barium sulfate is made to separate from a solution whose volume is 300 cc., which contains 1 gram potassium nitrate?

7. The solubility of  $\text{SrSO}_4$  in water is 0.097 gm. per liter. What weight of  $\text{SrSO}_4$  should be dissolved by 320 cc. of a solution which contains two gm. of  $\text{Na}_2\text{SO}_4$ ? Ans.  $3.72 \times 10^{-4}$ .

8. The solubility product of  $\text{PbSO}_4$  is  $1 \times 10^{-8}$  and of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ .

If a dilute solution of  $\text{Na}_2\text{SO}_4$  is added drop by drop to a solution which contains 0.1 gm. of  $\text{PbCl}_2$  and 0.154 gm. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and has a volume of 320 cc., will  $\text{PbSO}_4$  or  $\text{BaSO}_4$  separate first? What will be the concentrations of all the ions in the solution when sufficient sulfate ion has been added to cause the second salt to begin to separate? Disregard the slight increase in volume due to the sulfate solution added.

9. Outline as many procedures as you can suggest, which might be used to convert barium sulfate into barium nitrate.

10. What weight of sample should be used in order that each 5 mg. of  $\text{BaSO}_4$  found should represent one per cent of  $\text{SO}_4$  in the sample used for the analysis?

## CHAPTER XVI

### DETERMINATION OF MAGNESIUM IN MAGNESIUM SULFATE

#### I. Facts upon Which the Determination is Based

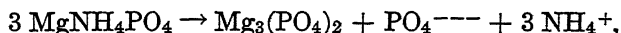
**General Features of the Method.** Magnesium is almost invariably determined by precipitating as  $\text{MgNH}_4\text{PO}_4$ , with either one or six molecules of water of crystallization, converting the precipitate into  $\text{Mg}_2\text{P}_2\text{O}_7$  by ignition, and weighing in this form. If a proper procedure is employed the method is entirely satisfactory, but appreciable errors may result from slight variations in the conditions of precipitation and subsequent treatment. This seems to be the result of the fact that phosphoric acid is a weak tribasic acid and neither magnesium oxide nor ammonium hydroxide is a strong base, and hence there is a decided tendency for the formation of a number of simple or double salts during precipitation and changes in the composition of these compounds during the filtration and washing of the precipitate. When such a precipitate is ignited, all of the magnesium originally present is not found in the form of pyrophosphate.

A large amount of experimental work, in which known amounts of magnesium were precipitated under varying conditions, has been carried out by a number of investigators, and several different procedures which give good results have been developed. The theory upon which these procedures is based has not been fully established owing to the difficulty of ascertaining with certainty the composition of the precipitates obtained and the concentrations of the ions actually present in the solutions from which these precipitates are separated.

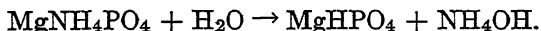
**Properties of Magnesium Ammonium Phosphate.** The transition temperature for the mono- and hexa-hydrates of this

compound has been shown<sup>1</sup> to be between 48° C. and 49° C. when in contact with water, and somewhat higher when in contact with solutions containing moderate concentrations of the electrolytes from which the precipitate was derived. When once formed, however, the monohydrate is only very slowly transformed into the hexahydrate below this temperature, and the hexahydrate only slowly into the monohydrate when above this temperature.

The solubility of the monohydrate at 22.7° C. in water was found to be 0.1076 gram of  $\text{MgNH}_4\text{PO}_4$  per liter when seventeen hours were allowed for saturation. The solubility of the hexahydrate, and of the hexahydrate associated with some of the monohydrate, was found to increase from 0.080 to 0.1352 gram per liter when the time allowed for a saturation of the solution was increased from sixty-nine hours to fourteen days, and the change was associated with a corresponding increase in the conductance of the solution. It was also found that the composition of the solid changed when washed with a large amount of water in that it lost ammonium ion and phosphate ion as compared with magnesium ion, in the ratio of  $3 \text{NH}_4^+$  to  $1 \text{PO}_4^{---}$ . These facts suggest that a reaction which should be represented by the equation,



takes place, and, since the change is probably a very slow one, this would explain the apparent increase in the solubility of the precipitate with the time allowed for saturation. This is a well known phenomenon, but it has usually been explained by assuming hydrolysis of the precipitate according to the equation



Several hydrates of  $\text{MgHPO}_4$  are known, but all of them are much more soluble than those of  $\text{MgNH}_4\text{PO}_4$ , and it seems probable that the solubility product of the compound  $\text{Mg}_3(\text{PO}_4)_2$  is attained in the solutions concerned before that of  $\text{MgHPO}_4$  is reached. It

<sup>1</sup> For most of the data quoted in this paragraph see the paper by Bube, *Zeit. für analytische Chemie*, 49, 562 (1910).



was also shown that the apparent solubility of the hydrates of  $\text{MgNH}_4\text{PO}_4$  was (a) decreased by the addition of  $\text{Mg}^{++}$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{---}$  or  $\text{HPO}_4^{--}$  but increased by  $\text{H}^+$ , (b) decreased by small, but increased by large concentrations of  $\text{NH}_4^+$ , (c) increased greatly by increasing temperature.

The physical properties of both the mono- and hexa-hydrates are entirely satisfactory. Both are easily obtained in crystalline form if conditions which cause them to separate slowly from solution are maintained, and in this form they are easily filtered and washed.

**Possible Sources of Error in the Precipitation.** Of the compounds which may separate along with the precipitate having the desired composition,  $\text{MgHPO}_4$  in various degrees of hydration is to be avoided. Since its formation clearly depends upon large concentrations of  $\text{HPO}_4^{--}$ , there is little probability that it will separate if the solution is sufficiently alkaline. Somewhat more  $\text{OH}^-$  than is necessary to give a basic color with litmus is necessary. A second possibility is the separation of  $\text{Mg}(\text{OH})_2$  whose solubility product is  $1.2 \times 10^{11}$ , but this is easily prevented by keeping  $(\text{OH}^-)$  at a moderate value. This is usually effected by adding sufficient ammonium chloride to buffer the solution, that is, prevent  $(\text{OH}^-)$  from reaching its limiting value.

A third source of error arises from the presence of a large concentration of ammonium ion, which causes low results. This has been attributed to the formation of  $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$ , which on ignition would decompose in accordance with the equation:



Such a change would not only give a low weight of precipitate, owing to loss of oxygen, but would result in still further losses during long continued ignition owing to the reaction,



since  $\text{P}_2\text{O}_5$  is slowly volatilized. There is, however, no convincing evidence for this theory. All attempts to prepare the compound  $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$  have failed, and the phenomena which have been outlined are equally well explained by assuming

that small amounts of the compound  $(\text{NH}_4)_3\text{PO}_4$ , of which at least two hydrates have been described, are occluded by the precipitate when the latter is made to separate from solutions containing large concentrations of  $\text{NH}_4^+$  and  $\text{PO}_4^{---}$ .

**Requirements of a Possible Method of Precipitation.** Since both of the hydrates of  $\text{MgNH}_4\text{PO}_4$  are easily converted into magnesium pyrophosphate by igniting at  $750^\circ\text{C}$ . to  $1000^\circ\text{C}$ ., precipitation might be made to take place under conditions which would yield either or both of these hydrates. Some chemists prefer to precipitate from a boiling solution, but there is no real advantage over precipitation at room temperature. Aside from the temperature, the important items to consider are the presence of a sufficient concentration of ammonium chloride to prevent the separation of magnesium hydroxide, and of ammonium hydroxide to prevent the separation of  $\text{MgHPO}_4$ . These conditions are satisfied if the total concentration of ammonium chloride or other ammonium salts equals 0.2, but does not exceed 0.5 molal and if ammonium hydroxide equals 1.0, but does not exceed 4 molal. The excess of precipitating agent added should not exceed 0.02 molal. It is also obvious that: first, the volume of the solution should be kept small, owing to the large solubility of the precipitate; second, the precipitate should be washed with dilute ammonium hydroxide, rather than with water; third, the precipitate should be allowed to stand, preferably over night, owing to supersaturation; and fourth, the precipitate should be made to separate slowly, preferably by the addition of very dilute ammonium hydroxide after the phosphate reagent has been added.

**Ignition of the Precipitate.** Complete conversion of the precipitate into the pyrophosphate is a slow process unless a crucible of moderate size is used and ignited by means of a blast lamp. It is sometimes difficult to heat a porcelain Gooch crucible to the necessary temperature and therefore paper filters are largely used. During the ignition a slight sintering takes place and, if a paper filter has been used, it is difficult to completely oxidize the organic matter derived from the paper. Care should be taken therefore to separate as much of the precipitate from the paper as is possible, burn the latter separately at a low temperature, and then add the main part of the precipitate. Even when

care is taken to insure conditions favorable to oxidation it is difficult to obtain a perfectly white precipitate. The error due to the small amount of organic matter which remains unoxidized when the precipitate is ignited under the proper conditions is negligibly small. The use of a platinum crucible for the ignition is to be avoided as such crucibles soon become brittle and develop cracks which render them useless. This is probably due to the formation of small amounts of phosphides, and cannot be prevented even when conditions favorable for complete oxidation of the precipitate are maintained.

## II. Details of the Method of Procedure

**Weighing and Precipitating.** The heptahydrate of magnesium sulfate, which is used for the determination, is easily obtained in a high degree of purity if crystallized from solution below 60° C.; above this temperature a hexahydrate may separate. If preserved in stoppered bottles away from direct sunlight, it can be kept indefinitely without loss of water and is the best primary standard for the study of methods for the determination of magnesium.

Place 3 to 4 grams of the pure dry salt in a clean sample tube and weigh out about 1 gram into a 200-cc. beaker. Dissolve this sample in 50 cc. of water, add 2 cc. of 6 N hydrochloric acid and 30 cc. of reagent sodium phosphate solution which contains 74.5 grams of  $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$  per liter, 1 cc. of which is equivalent to 0.005 gram of magnesium. Next add 6 N ammonium hydroxide slowly until the precipitate which forms temporarily disappears slowly, and then add it drop by drop with constant stirring till the solution is alkaline to a piece of litmus paper. Allow to stand for about five minutes and then add 20 cc. of 6 N ammonium hydroxide. Allow the mixture to stand for at least four hours, preferably over night.

**Filtration of the Precipitate.** Fold an 11-cm. filter paper to fit accurately a funnel of slightly larger size, and moisten with water. Decant the clear portion of the solution through the filter and then transfer the precipitate to the filter by means of a stream from a wash bottle, which contains one volume of 6 N

ammonium hydroxide mixed with four of water. Continue washing with this mixture until 20 cc. of the washings give no recognizable test for chloride ion when the proper reagents are added. Place the funnel containing the filter on a metal cone and allow to dry over the sand bath.

**Igniting and Weighing the Precipitate.** While waiting for the filter to dry, ignite and weigh accurately a small porcelain crucible. An 8-cc. crucible of the broad, rather than the narrow, form is to be preferred. As soon as the filter is perfectly dry, remove it from the funnel, separate the precipitate from it as far as possible, and carry out the further details of the ignition as directed on page 154. The final ignition should be made with a cover on the crucible using the full heat of a blast-lamp or a large Méker burner for at least a half hour and repeating until consecutive weighings, which do not differ by more than two-tenths of a milligram, are obtained. An effort should be made to obtain a pure white precipitate, but a slight amount of grayness, which does not disappear after a half-hour's ignition, signifies a negligibly small error only.

Calculate and report the percentage of magnesium present.

### III. Additional Information Regarding the Method

**Accuracy of the Method.** When it is possible to carry out this method under the ideal conditions of the procedure outlined above, results which do not differ from the correct value by more than one part in 300 are easily obtained, and, after some experience has been acquired with the method, much greater accuracy is attainable.

**Application to Other Classes of Substances.** In applying the method to other classes of substances, it is necessary to remove the very large number of cations which form insoluble phosphates in the presence of ammonium hydroxide and of large concentrations of ammonium ion. The latter can be eliminated by evaporating to complete dryness and volatilizing the ammonium salts by heating the residue to 250° C., or by evaporation with large amounts of nitric acid which slowly oxidizes the ammonium ion to oxides of nitrogen. Still another procedure which is very

satisfactory is to make a double precipitation. Although low results are obtained when  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is precipitated in the presence of an excessive concentration of ammonium ion, the separation of the magnesium seems to be complete. If therefore such a precipitate is separated and dissolved in a very small amount of hydrochloric acid, the magnesium can be precipitated from the resulting solution under ideal conditions.

Essentially the same requirements are demanded in the corresponding method for the determination of phosphate ion except that an excess of magnesium rather than of phosphate ion must be present. This procedure has extremely important commercial application in the evaluation of a variety of substances used in the fertilizer industry.

#### IV. Questions and Problems. Series 13

1. Calculate, at least approximately, the concentration of all the ions present in a solution in which magnesium is being determined exactly as outlined in the above procedure, after the mixture has stood for four hours.

*Ans.*  $(\text{Na}^+) = 0.118$ ,  $(\text{SO}_4^{--}) = 0.039$ ,  $(\text{PO}_4^{---}) = 0.0203$ ,  $(\text{Cl}^-) = 0.115$ ,  $(\text{NH}_4^+) = 0.115$ ,  $(\text{HO}^-) = 1.7 \times 10^{-4}$ ,  $(\text{NH}_4\text{OH}) = 1.07$ .

2. A solution known to contain about 0.05 gram of magnesium is given out for this determination. Give the details of procedure which should be used in order to make the conditions under which the precipitate separates identical with those of the procedure described.

3. Would you think it necessary to remove moderate concentrations of soluble salts of either Ag, Hg, Ca, Li, Fe Mn, Co, Cu, Pb, Cd, Na, or K before separating magnesium by this procedure?

4. What factors determine the completeness of the reaction which takes place when  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is ignited?

5. What reaction, if any, would you expect to take place during the ignition of (a),  $(\text{NH}_4)_3\text{PO}_4$ ; (b),  $\text{MgNaPO}_4$ ; (c)  $\text{NaH}_2\text{PO}_4$ , (d),  $\text{K}_2\text{HPO}_4$ ?

6. Write an equation representing a possible reaction for the oxidation of ammonium ion by nitric acid.

## CHAPTER XVII

### DETERMINATION OF IRON IN FERROUS AMMONIUM SULFATE

#### I. Facts upon Which the Determination is Based

**Composition of the Salt.** Ferrous ammonium sulfate is a double salt represented by the formula  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ . It is made by the evaporation of solutions containing about two moles of ammonium to one of ferrous sulfate, and can be obtained from dealers in a high degree of purity. As it slowly oxidizes, and in contact with dry air loses some of its water, even at  $25^\circ \text{C}$ ., it should be kept in a tightly stoppered bottle at a low temperature. If these changes have taken place, the crystals, instead of being transparent and of a pure green color, will lack transparency and show some degree of redness.

**Possible Methods of Procedure.** Ferrous iron can be precipitated as ferrous hydroxide and changed to the oxide by ignition, but it is never determined by such a procedure because ferrous hydroxide is (a) extremely difficult to filter and wash, (b) has a rather large solubility, and (c) is partially oxidized by direct absorption of oxygen during washing and ignition. The corresponding ferric compound is more easily filtered and washed, and is less soluble. Although it has been largely used in the quantitative determination of iron, the method lacks the high degree of accuracy often demanded owing to a slight reduction during ignition and to contamination of the precipitate with silica derived from the glass container. Although the volumetric methods discussed in Chapter XX are both simple and accurate, the gravimetric separation in the form of a metal by the use of an electric current has decided advantages in certain cases.

**Electrolytic Deposition of Iron.** The table of electrode potentials on page 160 states that the precipitation of iron from a molal

solution of ferrous ion requires 0.44 more volt than is needed for the reduction of hydrogen from a molal solution of hydrogen ion. The overvoltage required is roughly 0.141 while that required for hydrogen is almost negligible. It can be calculated from these data that the decomposition voltage of iron in a 0.045 molal solution, which corresponds to 0.25 gram of iron per 100 cc., is 0.62 volt while that required for deposition of hydrogen from a neutral solution is 0.413 volt. These figures clearly indicate the difficulty of separating iron from a neutral solution containing a normal ferrous salt; it is scarcely possible to effect complete separation from a solution in which water is decomposed at the anode and hydrogen ion accumulates in the solution as the precipitation progresses. A further difficulty is that some of the hydrogen necessarily liberated with the iron during the deposition is taken up by the latter and both increases its weight and makes it more brittle.

These difficulties are eliminated by causing the electrolysis to take place from solutions containing large amounts of ammonium salts of certain organic acids, especially oxalic, citric, and tartaric. Of these, ammonium oxalate is found to give the best results since, unlike the citrate and tartrate, the oxalate gives a precipitate which is practically free from carbon if proper procedure is used.

**Formation of Complex Oxalates.** The solubility of ferrous oxalate is only 0.077 gram per liter, but the addition of a soluble oxalate greatly increases its solubility, owing to the formation of a complex ion whose formula seems to be  $[\text{Fe}(\text{C}_2\text{O}_4^{--})_2]$ .<sup>1</sup> The constant which determines the formation of this ion, namely  $[\text{Fe}(\text{C}_2\text{O}_4^{--})_2] \div (\text{FeC}_2\text{O}_4) \times (\text{C}_2\text{O}_4^{--})$  has the value  $0.7 \times 10^3$ , and it is not surprising to find that at moderate concentrations the presence of 4 moles of soluble oxalate for every mole of ferrous iron prevents the separation of iron oxalate. The re-solution of ferrous oxalate, which has once separated in solid form, by the addition of a soluble oxalate is a slow process, and therefore it is preferable to add the iron solution to the oxalate rather than the reverse.

<sup>1</sup> Schafer, *Zeit. anorg. Chem.*, 45, 319 (1905).

**Changes During Electrolysis.** Electrolysis of a solution containing iron-oxalate ion yields at once a coherent deposit of pure gray iron at the cathode and oxygen and carbon dioxide at the anode. The deposition of iron results from the addition of electrons to the ferrous ions, small concentrations of which are present in the solution, which concentration is kept nearly constant by the gradual decomposition of the iron-oxalate ion present in much larger amounts. Unless the amperage used is kept very small, hydrogen gas will separate with the iron almost at the outset, and the time required for complete decomposition will be much greater than would be needed if simple ferrous ion only were present. The separation of large amounts of hydrogen is associated with important changes in the composition of the electrolyte. By causing the electrolysis to take place in a solution containing a large amount of ammonium oxalate and by the use of a cell provided with a diaphragm, it was shown<sup>1</sup> that the solution in the cathode compartment became basic owing to the accumulation of ammonia, and that oxalate ion was successively reduced to glyoxalate, glycolate, and succinate ion. The formation of succinate ion was associated with the separation of amorphous carbon and carbon dioxide in equivalent amounts and very small amounts of carbon monoxide. Practically no carbon was separated during the first two hours of the electrolysis and a pure precipitate of iron was obtained if the electrolysis was stopped as soon as the concentration of the iron had been reduced to a negligible value. Another effect was the precipitation of a small amount of ferrous hydroxide owing to the accumulation of hydroxyl ion, but this gradually dissolved with the accumulation of succinic ion. Similar effects were obtained when no diaphragm was used but at a much slower rate of speed. At the anode much of the oxalate ion is oxidized to carbon dioxide and small amounts of ferric to ferrous ion, but since ferric ion forms also a complex iron-oxalate ion it is not precipitated and is slowly reduced to the metal at the cathode.

The data needed for the calculation of the minimum voltage needed are not available. Good deposits are obtained with as

<sup>1</sup> Sontag, *Zeit. f. Elektrochemie*, 30, 333 (1924).



much as one ampere, provided gauze electrodes exposing 80 to 100 sq. cm. of surface are used. With solutions of moderate concentration this requires about 3.5 volts and gives complete deposition of 0.2 gram of iron in two hours. Electrolysis under these conditions is associated with a considerable rise in temperature, but this is not objectionable. The deposited iron is not acted upon appreciably by the residual solution, but is easily oxidized by the air if the temperature is high. It is desirable to wash the cathode with alcohol and dry it at 60° C.

## II. Outline of the Method of Procedure

**Splitting a Watch Glass.** The large amount of gas liberated from both anode and cathode during this electrolysis may result in appreciable mechanical loss of the solution, and it is desirable, therefore, to cover the containing vessel with the two halves of a watch glass. A glass which is not too thick is easily divided into halves by making a scratch on its convex surface with a steel or diamond glass cutter, using a piece of cardboard for a straight edge, and then bringing the glass along the scratched line into contact with a piece of fine nichrome wire, which is heated to redness by means of an electric current. If the glass does not fall apart at once place a drop of cold water on the glass near the end of the scratch.

**Preparation of the Solution.** Weigh out about 1.5 grams of the ferrous salt into a 150-cc. beaker, add 50 cc. of water and stir until dissolved. Weigh out roughly 6 grams of crystallized ammonium oxalate into a 200-cc. beaker, add 50 cc. of water, warm and stir till most of the salt is dissolved. Pour the iron solution into the oxalate solution and rinse the beaker with at least four 5-cc. portions of water. The resulting solution should be perfectly clear and of a deep yellow color.

**Electrolysis of the Solution.** Ignite a clean platinum gauze electrode, whose surface area is at least 60 cm., to dull redness; allow to cool without placing in a desiccator, and weigh accurately. Place the cathode in the iron solution and the anode in the center of the gauze cylinder. Carry the beaker to the bench containing an installation similar to that represented in Fig. 40. Throw

the ammeter and voltmeter switches opposite one of the vacant electrolytic stands to the point marked 1, and turn the arm of the adjustable rheostat well over to the left of the center as shown in the figure. Connect the cathode with the lower arm of the electrolytic stand and the anode with the upper, carefully

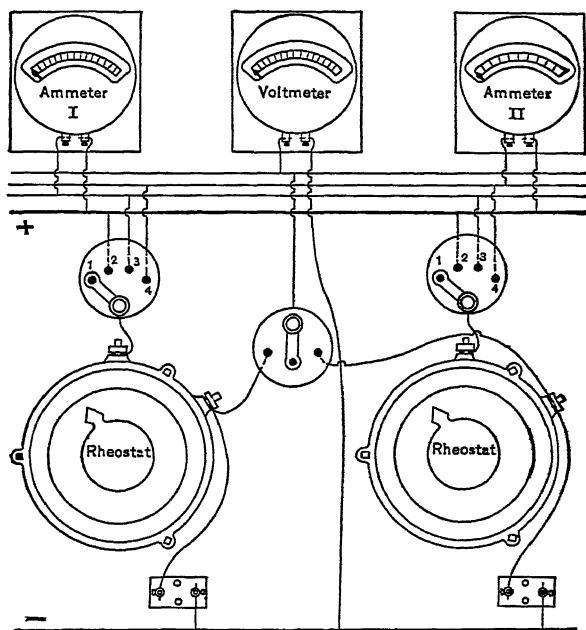


Fig. 40.—Plan of wiring of bench for electrolytic determinations.

adjusting both electrodes so that both extend to the bottom of the beaker.

Next note whether the needle of the ammeter at the left, that is the one reading up to 15 amperes, stands at zero, which means that this instrument is not being used on any of the other circuits, and, if not at zero, wait until it is out of use. As soon as the pointer of the instrument stands at zero, throw the ammeter switch to the point marked 3 and turn the arm of the rheostat till the instrument shows that a current of 1 ampere is flowing through the circuit; then throw the ammeter switch back to the

point marked 2. Next turn the voltmeter switch to the point nearest the circuit in use and after recording the reading of the needle return the switch to the central point. At the end of forty-five minutes the solution should be colorless, but electrolysis should be continued for some thirty minutes beyond this time.

**Washing and Weighing the Cathode.** Fill a 200-cc. beaker with distilled water and place on the desk near the solution; raise the electrolytic stand without breaking the circuit and plunge the electrodes without loss of time into the beaker of water. Add to the beaker containing the residual solution 5 cc. of concentrated hydrochloric acid and about 5 cc. of potassium ferri-cyanide solution. If it gives a perceptible reaction for iron the determination should be repeated. If no iron is found in the solution, disconnect the cathode and rinse in alcohol, using first the cylinder marked "for first washing" and then the cylinder marked "for second washing," which should contain 98 per cent alcohol, and drain on a piece of filter paper. Dry in an air bath for a few minutes at a temperature not exceeding 60° C. and weigh. Do not allow the alcohol on the cathode to take fire; if it does so the precipitated iron will also burn and the heat liberated may cause some of it to alloy with the platinum and spoil the electrode.

Place the cathode in the cylinder containing dilute hydrochloric acid and allow to remain there until absolutely all the deposited iron has been dissolved, that is, till no more hydrogen gas is liberated. Then remove and wash with distilled water. Calculate and report the percentage of iron found.

**Further Details Regarding the Method.** Ferric ion also forms a complex with oxalate ion and the procedure outlined above yields equally satisfactory results if all the iron is in the ferric form, although the time required for deposition is slightly increased. The presence of chloride or nitrate ion in small amounts has no effect upon the results.

Obviously the method is inaccurate in the presence of metals whose decomposition voltages are smaller than that of iron and which are not precipitated by an excess of oxalate ion. These include copper, cobalt, nickel, and many others. Manganese is not objectionable if present in small amounts only, since it is

oxidized at the anode partly to permanganate ion and partly to manganese dioxide. Aluminum in small amounts is not objectionable if the electrolysis is not continued too long. The accumulation of hydroxyl ion in the solution finally causes the separation of aluminum hydroxide and contamination of the precipitate unless it is kept in solution by the addition of a small amount of oxalic acid. Chromium is not objectionable as it is oxidized at the anode to chromate ion.

### III. Questions and Problems. Series 14

1. Show by means of a simple diagram the direction of flow of electrons during electrolysis when the ammeter switch is (a) at the point 2 of Fig. 40, (b) at the point 4, (c) when the voltmeter switch is at such a position that the voltage is registered.

2. Calculate by means of Faraday's Law how long a time would be required to deposit all the iron present in 1 gram of ferrous ammonium sulfate if a current of 0.5 ampere was used. Why is this calculation of no significance?

*Ans.* 16.45 minutes.

3. If the electrode potential of ferrous ion at molal concentration is  $-0.44$  volt; what would it be in a 100-cc. solution which contained 0.0001 gram of ferrous ion?

*Ans.*  $-0.58$  volt.

4. In preparing the solution for electrolysis what is the objection to adding the oxalate solution to the iron solution? Why is hydrochloric acid added before the residual solution is tested for unprecipitated iron by means of potassium ferriocyanide?

5. Enumerate all the items which determine the minimum voltage needed for the separation of iron from the solution prepared as directed above.

6. Give the equations representing the successive reduction of oxalate ion to glyoxalic, glycolic, and succinic acids.

7. Outline an electrolytic method for the determination of iron in a sample of iron wire, and give all the reactions made use of. Assuming that the sample contained small amounts of manganese, sulfur, phosphorus, silicon, graphite, and combined carbon, would you anticipate an accurate result?

## CHAPTER XVIII

### ANALYSIS OF BRASS

#### I. Facts upon Which the Analysis is Based

**Composition of the Alloy.** The essential constituents of this alloy are copper and zinc. Most samples contain at least 50 per cent of copper. Of the less important constituents, lead, which makes the alloy work better in a lathe, and tin, which increases its hardness, are frequently present, sometimes as much as 5 per cent. Several other metals, especially iron, manganese, and antimony are often present in smaller amounts and usually represent impurities in the component metals. It will be assumed that the percentages of these last named substances are negligible in the procedure outlined below.

A representative sample can usually be obtained by drilling a hole in the ingot or bar, or by cutting thin shavings from it on a lathe; the drillings or shavings should be carefully examined for particles of wood or foreign metals with which they may be contaminated.

**Separation of Tin as Metastannic Acid.** The salts of tetravalent tin are easily hydrolyzed, largely owing to the very slight solubility, even in strong acids, of one of the resulting products which is known as metastannic acid. The composition of this substance is usually represented by  $(\text{H}_2\text{SnO}_3)_n$ . Its solubility and other properties vary appreciably according to the method of preparation, and it is probable that the differences are due to variations in the relative proportions of water and stannic oxide of which it is composed. Similar compounds,<sup>1</sup> resulting from the action of soluble hydroxides on stannic salts, are soluble in acids,

<sup>1</sup> Collins and Wood, J. Chem. Soc., 23, 324 (1881); Zeit. anorg. Chem., 23, 111 (1900).

but the action of acids, especially nitric acid, on metastannic acid is very slight. It possesses pronounced colloidal properties and in the absence of moderate concentrations of a strong electrolyte is easily peptized. It also possesses to a marked degree the ability to adsorb a variety of other substances, especially ferric iron, and phosphoric and arsenic acids.

The dissolution of tin-containing alloys with nitric acid, removal of the excess of acid by evaporation, and dilution of the residual solution insures complete separation of the tin as metastannic acid. This treatment also converts any antimony present into insoluble antimony tetroxide, and causes partial separation of ferric, phosphoric, and arsenic ion, as well as slight precipitation of nearly all the other metals present, such as copper, lead, and zinc, by adsorption.

Metastannic acid is slowly but completely converted into stannic oxide by heating to 500° C. It is easily reduced by organic matter even at moderate temperatures.

**Separation of Lead as Sulfate.** The solubility of pure lead sulfate in water is 0.044 gram per liter; it is reduced by the addition of sulfuric acid up to the point at which the mixture contains about 10 per cent by volume of concentrated acid, but beyond this concentration the solubility increases. The solubility is also increased somewhat by the presence of even small concentrations of hydrochloric and nitric acids, but is greatly decreased by the presence of even small percentages of alcohol.

The density of the pure precipitate is 6.23 grams per cc. and, although a typical pulverulent precipitate, it settles readily and does not occlude other salts badly. No difficulty is experienced in separating as much as 1 gram of the precipitate on an ordinary filter paper. It can be heated to 400° C. with little danger of decomposition, but it is easily reduced by organic matter, even at moderate temperatures. As the metal is appreciably volatile, great care should be taken to avoid reduction.

**Electrolytic Separation of Copper from Zinc.** Since the electrode potential  $\text{Cu}^{++} \rightarrow \text{Cu}$  is represented by  $-0.344$  volt, while that of  $\text{Zn}^{++} \rightarrow \text{Zn}$  is represented by  $+0.758$  volt, it should be possible to completely precipitate copper free from zinc with an electric current by either the constant voltage or the constant

current procedure. Furthermore, metallic copper can be made to separate in a dense coherent form from either acidic solutions or from solutions containing an excess of ammonium hydroxide, provided the current density is not excessive. Separation in the presence of both hydrogen and nitrate ion yields the smoothest and densest deposits, but the oxidizing properties of this mixture make the separation of the last few milligrams of copper difficult, and the danger of re-solution of some of the precipitated copper while the electrode is being washed is large. These difficulties are eliminated by the substitution of sulfate for nitrate ion, but greater care must be taken to avoid large current densities, a high temperature, and poor circulation, else the precipitated copper may be spongy or powdery. If a foil electrode is used, it is not advisable to employ more than 0.0005 ampere per square centimeter, but if a gauze electrode is used the current density may be increased to 0.01 ampere per square centimeter.

**Separation of Zinc as Phosphate.** Zinc, like magnesium, forms a number of insoluble phosphates, and, like that element, can be precipitated as a phosphate of definite composition, but under conditions which are very different from those required for the quantitative precipitation of magnesium. When a soluble phosphate is added to a neutral solution of a zinc salt, which also contains a large concentration of an ammonium salt, a flocculent precipitate, whose composition is not definitely known but may be  $\text{Zn}_3(\text{PO}_4)_2$ , separates. If this precipitate is digested at  $60^\circ \text{C}$ . for a few minutes, it is converted into a dense crystalline precipitate whose formula is  $\text{Zn}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$ . Like the corresponding magnesium compound this precipitate is readily soluble in solutions containing even small concentrations of hydrogen ion. Unlike the magnesium compound it is readily soluble in solutions containing small concentrations of ammonium hydroxide, owing to the formation of the complex zinc-ammonium ion. Further, it does not hydrolyze as easily as the magnesium compound and can be washed with pure water with but little loss. It is evident, therefore, that the quantitative separation of zinc as phosphate requires careful neutralization of the solution. Actual precipitations of known amounts of zinc have also shown that the solution should contain from eight to ten times the theoretically required

amount of phosphate ion where the total amount of zinc present is about 0.2 gram and the total volume is 200 cc. A large excess of phosphate ion and ammonium ion seems to assist in causing the precipitate to crystallize.

The crystalline zinc ammonium phosphate readily loses all of its water at 105° C. and is not appreciably hygroscopic. It can also be converted into the pyrophosphate on direct ignition, but, as with the corresponding transformation of the magnesium compound, it fuses at a bright red heat and is partially reduced by organic matter.

## II. Outline of the Method of Procedure

**Decomposition of the Sample.** Weigh out 3 grams of sample into a 100-cc. beaker, add 25 cc. of dilute nitric acid, and cover with a watch glass. Action should begin to take place almost at once and complete disintegration should be effected within a few minutes unless the sample includes coarse particles of alloy. If the action is too slow, warm the beaker; if at any time it becomes too violent, place the beaker in cold water or add a small amount of cold water to it. As soon as the alloy is completely disintegrated, remove and rinse off the watch glass cover, place on the steam bath, and allow to evaporate almost to dryness, that is, till a large amount of bluish green solid appears. Treat the residue, which consists of insoluble basic nitrates or hydrated oxides of the metals present, with 5 cc. of dilute nitric acid, stir for a few minutes, then add 25 cc. of water, and digest till the small amount of residue, if any remains, is pure white and finely divided.

**Determination of Tin.** Filter the residual precipitate of metastannic acid, which may also contain small amounts of antimony tetroxide and occluded copper and lead, on a small filter and wash with nitric acid of about molar strength till free from soluble salts, then once with water, and dry. As the precipitate is usually very fine and rapidly fills up the pores of the paper, filtration is slow and a second filtration of the first portion of the filtrate is sometimes necessary. Place the filter in a small porcelain crucible, smoke off the volatile matter at a low temperature, and ignite till the carbon is entirely consumed. Allow to cool, moisten



the residue with a single drop of concentrated nitric acid, cautiously evaporate to dryness, preferably on the steam bath, then ignite, cool, and weigh. Calculate and report the percentage of tin present from the stannic oxide found. Pure stannic oxide is yellow when hot and white when cold, but the precipitate usually obtained in this analysis is somewhat yellow even when cold owing to occluded metals, especially iron.

**Determination of Lead.** Add to the filtrate from the meta-stannic acid 7 cc. of concentrated sulfuric acid and evaporate till white fumes of sulfur trioxide are given off. They will not appear until the temperature of the mixture reaches  $250^{\circ}\text{C}$ . and the volume is reduced to about 7 cc.; they may also be identified by their very unpleasant effect upon the throat and by the fact that they appear at the surface of the evaporating liquid as well as at the mouth of the beaker. During the evaporation a voluminous precipitate composed of the sulfates of copper, zinc, and lead separate, which makes it necessary to use extreme care to avoid losses from spattering (see page 37). Allow the beaker to cool, cover with a watch glass, cautiously introduce 50 cc. of water, and stir until the small amount of finely divided precipitate, if any remains, is pure white. Then set aside for a half hour. While waiting, prepare and weigh accurately a Gooch crucible. Connect the crucible with a clean filter flask, filter the precipitate of lead sulfate on it, wash four times with a mixture of equal parts of dilute sulfuric acid and water and twice with 20 per cent alcohol. Heat the crucible slowly to a temperature of  $250^{\circ}\text{C}$ ., cool, and weigh accurately. Calculate and report the percentage of lead present.

**Division of the Solution.** Transfer the filtrate from the lead sulfate to a 250-cc. graduated flask, dilute till the lowest part of the meniscus corresponds to the line on the neck of the flask, place a rubber stopper in the mouth of the flask, and mix thoroughly by alternately inverting and rotating the flask. Measure out three 50-cc. portions of the solution as follows: first pour 20 cc. of the solution into a small beaker, use this to rinse out a clean but not necessarily dry 50-cc. pipette, and discard the solution used. Next, suck up a further quantity of the liquid into the pipette until it rises above the mark on the stem, and allow to

drain back into the flask until the lowest point on the curve of the meniscus corresponds to the mark on the stem of the pipette. Then remove the pipette from the flask and allow the solution to flow into a clean 150-cc. beaker and to drain for two minutes, but do not rinse out with water. Calculate the actual weight of the original sample represented by the fraction of the solution measured out from the ratio between the corrected capacity of the pipette and flask. See Chapter XXVIII for further explanation of the details of the measurement.

**Determination of Copper by Electrolysis.** To one of the 50-cc. portions of the solution which has been set aside add sufficient ammonium hydroxide to redissolve the copper and zinc hydroxides which usually separate. A very small precipitate of iron may remain; if the amount is large it should be filtered off, redissolved in acid, and reprecipitated; if left in the solution it will separate with the zinc when it is precipitated. If the sample is known to contain an appreciable amount of iron, it should be separated by double precipitation with ammonium hydroxide after separation of the lead sulfate.

Ignite and weigh accurately a clean platinum gauze electrode, place it in the copper-zinc solution, add 2 cc. of concentrated sulfuric acid and enough water to cover the electrode. Introduce a spiral anode and connect with one of the sets of terminals at the electrolytic bench. Change the resistance of the circuit by means of the rheostat (see page 176) till a current 0.8 ampere is passing through the solution. Allow the electrolysis to continue for at least twenty minutes after the solution has become colorless. If both electrodes are made to touch the bottom of the beaker, and if the total volume of the solution does not exceed 80 cc., the time required for complete precipitation should not exceed one hundred minutes. A thin film of brown or black color sometimes separates on the anode; it is usually due to lead dioxide derived from the small amount of lead ion still in the solution. It may be manganese dioxide, but usually the presence of manganese is shown by the pink color of the permanganate ion around the anode.

Place a small beaker, containing sufficient water to cover the cathode, on the bench near the solution being electrolyzed, raise the stand supporting the electrodes, and, without disconnecting

the attached wires, plunge the electrodes into the water. Allow the current to pass for a few minutes, rinse the electrodes by rotating the beaker, then disconnect the cathode, remove from the water and allow to drain and absorb as much of the water as possible on a piece of filter paper. Rinse the cathode in 95 per cent alcohol, absorb the excess of alcohol on a filter paper, and dry it about 50° C. by holding it over a hot sand bath for a few minutes. Weigh accurately and calculate the percentage of copper present.

**Determination of Zinc.** Transfer the solution from which the copper was precipitated to a 300-cc. beaker, and rinse out with the solution used to rinse the cathode. Add dilute ammonium hydroxide until a drop of the solution shows a barely perceptible basic reaction when used to moisten a narrow strip of litmus paper, then heat to about 60° C. and add 35 cc. of ammonium phosphate solution, which should give a flocculent white precipitate. Heat the solution almost to the boiling point and keep at this temperature until the flocculent precipitate has become granular and settles rapidly. As this change progresses and the precipitate becomes denser, there is some danger of mechanical loss unless the mixture is stirred. Again test the solution with litmus paper and add either very dilute ammonium hydroxide or hydrochloric acid till the solution does not affect either red or blue litmus paper. Set the mixture aside for a half hour and, while waiting, prepare and weigh a Gooch crucible.

Filter the precipitate on the crucible, wash with cold water till free from soluble salts, dry at 105° C. in an oven, cool, and weigh accurately. Calculate the percentage of zinc present, assuming the precipitate is pure  $\text{Zn}(\text{NH}_4)\text{PO}_4$ .

The two remaining portions of the original brass solution may be used in checking the results for copper and zinc.

**Additional Suggestions.** If the sample is known to be free from tin and lead, the procedure outlined above may be greatly abbreviated by decomposing with dilute nitric acid and evaporating at once with a slight excess of sulfuric acid. With such samples there is no decided advantage in weighing out a large amount of sample and taking an aliquot part of the solution for the determination of copper and zinc. It will be found that the evapora-

tion with sulfuric acid is much more easily effected if only 0.6 or 0.7 gram of sample is used.

If the amount of tin precipitate is large, the error from occlusion becomes too large to be disregarded. It is best purified either by digesting the recently precipitated metastannic acid with a strong solution of ammonium sulfide or by fusing the ignited precipitate with a mixture of equal parts of sulfur and sodium carbonate and digesting the fused mass with water. This treatment separates the tin and antimony from iron, manganese, lead, copper, and zinc.

### Questions and Problems. Series 15

1. In this analysis what change, if any, would it be desirable to make in the volume of sulfuric acid added before evaporation if (a) the amount of sample used were increased to 5 grams, (b) the amount of nitric acid used to dissolve the sample were increased, (c) the relative amounts of copper and zinc in the sample varied?

2. Suggest formulas for all possible compounds which might be expected to separate when solutions containing copper sulfate, zinc sulfate, and sulfuric acid are evaporated.

3. What other metals should separate with the copper under the conditions used in the procedure outlined above?

4. Suggest a procedure for the determination of tin in this alloy by an electrolytic process, and point out some of the advantages and disadvantages.

5. Explain how the addition of sodium hydrogen phosphate to a neutral solution containing zinc and ammonium salts might increase the concentration of hydrogen ion in the solution.

6. Name all the factors which would determine whether copper would be precipitated when a solution of di-sodium hydrogen phosphate was added to a solution made by adding a slight excess of ammonium hydroxide to a solution of cupric sulfate.

7. How would you prepare a solution whose composition is the same as that of the filtrate from the zinc precipitate, in the analysis described above, assuming that 3 grams of a sample composed of 65 per cent copper and 35 per cent of zinc was used, and one-fifth of it used for determining copper and zinc?

8. Write the electrode half-cell reactions for the electrolysis at low-current density of concentrated sulfuric acid with (a) platinum electrodes, (b) lead electrodes.

9. Write the reactions which should take place (a) when metastannic acid is treated with a solution of sodium sulfide, (b) when stannic oxide is fused with a mixture of sulfur and sodium carbonate.

## CHAPTER XIX

### SEPARATION OF CALCIUM FROM MAGNESIUM AND PARTIAL ANALYSIS OF LIMESTONE

#### I. Facts upon Which the Analysis is Based

**Composition and Uses of Limestone.** This rock invariably contains, in addition to calcium and magnesium carbonates, small amounts of the carbonates and oxides or hydrated oxides of iron, manganese and aluminum, and more or less quartz, clay and other silicates. The minerals pyrite, graphite, apatite and gypsum are frequently associated with limestone.

This analysis forms one of the problems frequently presented to the analyst since limestone is an essential raw material in many branches of chemical technology. The complete analysis takes much time and labor, and for many technical uses is unnecessary; hence in many factories it is customary to make a more rapid "proximate analysis," in which certain groups of constituents, which are present in small amounts only, are separated and reported as a whole, rather than being resolved into their ultimate elements.

**Proximate Method of Analysis.** If the sample is treated with nitric or hydrochloric acid the quartz, graphite and most of the silicates remain undissolved. If the amount of insoluble matter left is very small it is frequently ignited, which effects combustion of the graphite, weighed and reported as "gangue" or "insoluble matter." If the amount present is larger it is usually considered necessary to treat the sample as an insoluble silicate (see Chapter XXI), or to treat the gangue which has been separated as an insoluble silicate.

The iron, aluminum, and phosphoric acid present in the acid solution are almost invariably separated from the other bases

present by the use of ammonium hydroxide, and the entire precipitate weighed and reported as mixed oxides. Following the ammonium hydroxide precipitation bromine is frequently used to separate the manganese as hydrated dioxide, but the precipitation is far from complete unless the ammonium salts present are first eliminated.

The loss which results from ignition represents still a third group of constituents of which carbon dioxide is by far the most important. The determination of the percentage loss on ignition is sometimes substituted for the more accurate estimation of the carbon dioxide present.

After the elimination of all the elements named only calcium and magnesium remain. As the percentages of these elements often have an important practical significance they are usually determined with considerable care and accuracy.

**Sources of Error in the Determination of Gangue.** This determination furnishes an illustration of a solution process dependent upon the chemical action of a reagent (see Chapter XXII). Since certain silicates, such as clay, are but slowly acted upon by the acids used the results obtained depend to some extent upon the fineness of the sample, the length of time it is treated, and the composition of the acid used. There is no generally accepted standard method of procedure. Sufficient nitric acid should be present to dissolve any pyrite and to effect complete oxidation of the iron. After decomposition has been effected the solution should be evaporated to complete dryness to dehydrate and render insoluble the silicic acid formed (see Chapter XXI).

**Sources of Error in the Determination of Iron and Alumina.** Ferric hydroxide and aluminum hydroxide form bulky precipitates, which are extremely difficult to filter and wash. When separated by the addition of ammonium hydroxide from a solution which also contains calcium and magnesium, the resulting precipitate invariably contains these elements also, even though a large amount of ammonium chloride was present. This is due in part to the difficulty of washing the precipitate and to occlusion; it may also result from the absorption of carbon dioxide by the reagent before use, or by the mixture after precipitation, and formation of insoluble calcium carbonate.

Ammonium hydroxide acts upon glass, especially the ordinary soft glass, appreciably, and solutions which have stood in bottles for some time invariably contain a scale-like precipitate which is largely composed of silica; it can be removed by filtration, but the filtered solution may still contain small amounts of soluble silica, some of which may separate when the reagent is used. Hence when results of the greatest accuracy are demanded this precipitation must be made in vessels of resistant glass or still better of platinum, and the ammonium hydroxide used must be freshly distilled. In commercial work the only precaution usually taken is to filter the reagent, and to reduce its concentration and the time it is in contact with the containing vessel to a minimum.

The hydroxides of iron and aluminum are converted into the corresponding oxides at a temperature of about  $600^{\circ}\text{C}$ . and much higher temperatures can be used without danger of further changes. Ferric oxide is easily reduced to lower oxides by organic matter at this temperature.

**Properties of Calcium and Magnesium Oxalates.** Crystalline calcium oxalate ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) dissolves in water to the extent of 6.7 mg. per liter. If precipitated from an alkaline solution it is finely divided and bulky, but if precipitated from an acid solution it is coarsely crystalline. It occludes magnesium, and to a less extent sodium, potassium and ammonium salts, probably as the result of its tendency to form double salts of these metals. The amount of occlusion is reduced by precipitating from a solution containing a slight excess of free acid; under such conditions, however, the precipitation is incomplete and although about 80 per cent can be separated from a solution which is distinctly acid, the remainder must be separated from a solution which is distinctly alkaline. For these reasons it is decidedly preferable to separate most of the precipitate by the addition of a solution of oxalic acid to the neutral or barely acid calcium-containing solution, and the balance by neutralizing the resulting mixture. A reagent which contains 45 grams of crystallized oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) per liter (1 cc. of which is equivalent to 0.02 gram of  $\text{CaO}$ ) is a convenient one to employ.

Magnesium oxalate ( $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) is soluble in water to the extent of 300 mg. per liter, but shows a remarkable tendency

to form supersaturated solutions, so that the apparent solubility may rise to three hundred times the normal value. Supersaturated solutions of this kind deposit a large part of the excess of dissolved salt rapidly, but much of it is retained in solution even after long standing.

Calcium is not completely precipitated from solutions containing large amounts of magnesium salts unless an excess of oxalate ion is present. If sufficient oxalate ion is present to combine with both the calcium and magnesium present the precipitation is complete; excessive concentrations of oxalate ions must be avoided to prevent the solution from becoming supersaturated with respect to magnesium oxalate.

The properties of these oxalates which are enumerated above make it necessary to adopt and adhere to certain definite conditions in separating calcium from magnesium. The weight of oxalic acid used, as compared with the weights of calcium and magnesium present, and the total volume from which the precipitate is made to separate, are of especial importance. The directions which are given below are especially designed for the analysis of limestone;<sup>1</sup> they also apply to samples in which the proportion of magnesium to calcium is much greater than that found in limestone provided the amount used is sufficient to furnish a total weight of 0.4 gram of the two oxides.

**Theory of Separation of Calcium from Magnesium.** The occlusion of magnesium by calcium oxalate has been made the subject of many investigations. It was shown by Richards<sup>2</sup> that the error from this source could be greatly reduced by the presence of large concentrations of ammonium ion or of small concentrations of hydrogen ion. He attributed the beneficial effect of hydrogen ion to the repression of the ionization of oxalic acid, and assumed that reduction in the concentration of the oxalate ion must reduce the concentration of ionized magnesium oxalate and therefore of the occluded magnesium oxalate. He attributed the beneficial effects of large concentrations of ammonium ion to reduction in the concentration of simple magnesium ion owing to the formation of a magnesium ammonium complex,

<sup>1</sup> Jour. of Amer. Chem. Soc., 31, 918 (1909).

<sup>2</sup> Proc. Am. Acad. of Arts and Sciences, 36, 375 (1901).



and subsequent reduction in the concentration of unionized magnesium oxalate. The evidence for the formation of such a complex is not conclusive. As large amounts of ammonium ion, which seriously affect the subsequent separation of the magnesium, must be used in order to reduce the error from occlusion to a negligible amount, it is preferable to separate the calcium from solutions containing small concentrations of hydrogen ion, which, as already noted both reduces the error from occlusion and greatly improves the character of the precipitate.

**Weighing the Calcium Precipitate.** Although crystallized calcium oxalate loses most of its water at  $200^{\circ}\text{C}$ ., it is difficult to expel all of it without causing some of the precipitate to decompose into calcium carbonate and carbon monoxide, which is not a reversible process. It can be completely changed into the carbonate by heating for a long time at  $400^{\circ}\text{C}$ . or into the oxide by heating at  $850^{\circ}\text{C}$ . As the oxide rapidly absorbs both water and carbon dioxide it must be weighed in a covered crucible as rapidly as possible.

**The Separation of Magnesium.** The filtrate from the calcium has a large volume and contains a large amount of ammonium chloride and some ammonium oxalate. These conditions make it necessary to modify somewhat the method used in Chapter XVI. The large concentration of the ammonium ion greatly retards the separation of the precipitate and gives it an abnormal composition. Hence it becomes necessary to concentrate the solution, to make a preliminary precipitation in which the precipitate is allowed to stand for ten hours, to separate and redissolve this precipitate and to make a final precipitation as in the analysis of magnesium sulfate.

## II. Outline of Method of Procedure

**Composition of the Sample Used.** It will be assumed that the sample used for this analysis contains only negligible amounts of manganese, phosphoric acid and sulfur. Qualitative tests for all of these elements should be made while the rest of the analysis is being carried out, by the following methods.

Test for manganese by dissolving about 1 gram in 5 cc. of

dilute hydrochloric acid, evaporating almost to dryness with 10 cc. of dilute nitric acid, again dissolving in 5 cc. of dilute nitric acid, filtering, diluting to 50 cc., adding about a half gram of sodium bismuthate and warming to 50° C. If manganese is present the pink color of permanganic ion, whose intensity is proportional to the amount of manganese present, will appear.

Test for phosphoric acid by dissolving about 1 gram in 5 cc. of dilute nitric acid, evaporating to dryness, again dissolving in 5 cc. of nitric acid, filtering and diluting to 50 cc., adding 10 cc. of reagent ammonium molybdate and warming to 50° C. If phosphorus is present it is precipitated quantitatively as a yellow pulverulent precipitate whose composition is represented approximately by the formula  $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MoO}_3$ .

Test for sulfur by treating 1 gram of sample as in the analysis of pyrite, being very careful to wash the gangue matter with a large amount of hot water to dissolve separated calcium sulfate. It is not necessary to reduce the iron before adding barium chloride.

**Separation of the Gangue.** Weigh out about 0.7 gram of the finely ground sample into a 200-cc. beaker, cover with a watch glass and gradually introduce 20 cc. of dilute hydrochloric and 5 of dilute nitric acid. When violent action ceases, heat the beaker on a steam bath long enough to insure complete decomposition, that is, until no more gases are liberated. Then remove the watch glass, rinsing off the under surface with a stream from a wash bottle, and evaporate to complete dryness. To the residue add 10 cc. of dilute hydrochloric acid and digest five minutes, or until the basic salts or oxides which may have formed have been entirely dissolved. Add 20 cc. of water, filter through a 7-cc. filter, wash four times with 10-cc. portions of water and drain. Place the still moist filter in a weighed crucible and heat cautiously over a wire gauze until the water has been expelled and the paper consumed; finally ignite over a direct flame for about ten minutes, then cool and weigh accurately. Calculate and report the per cent of gangue present.

**Separation of Iron and Aluminum.** Warm the filtrate from the gangue and add to it slowly and with constant stirring recently filtered ammonium hydroxide until the solution smells distinctly

of the reagent. Place the beaker on the sand bath and keep at a temperature slightly below the boiling point for about ten minutes or until the odor while still easily recognizable is not unpleasantly strong. This should cause the separation of a small amount of a precipitate whose color may vary from red-brown to white; if it is dark brown or black it indicates that manganese is present in it, probably because the concentration of ammonium chloride in the solution was too small. Filter on a 7- or 9-cm. filter and wash with water containing about 20 grams of ammonium chloride per liter, which prevents the aluminum hydroxide from forming a hydrosol. Redissolve the precipitate in a small amount of warm dilute hydrochloric acid and dilute to 50 cc.; reprecipitate, filter and wash as before, receiving the filtrate in the beaker containing the first filtrate, and acidify with hydrochloric acid. Treat the precipitate finally separated like the gangue matter; calculate and report the total percentage present.

**Determination of Calcium.** Bring the combined filtrates from the two ammonium hydroxide precipitations to a volume of about 300 cc., add a drop of methyl orange indicator and sufficient ammonium hydroxide to change the color from pink to salmon yellow. Heat to boiling and add slowly, with constant stirring, 22 cc. of oxalic acid solution, set aside for ten minutes, then add very slowly, that is, over an interval of at least five minutes, 3 cc. of ammonium hydroxide which has been diluted to 30 cc. with water. If this does not make the solution distinctly alkaline add a further quantity of the reagent in the same manner. After the precipitate has stood for an hour filter through a 9-cm. filter and wash with water until free from chlorine. Place the filter in a porcelain or platinum crucible which has been weighed with its cover, and destroy the filter as in the determination of gangue; finally, heat the crucible over a Méker or Chad-dock burner for at least twenty minutes. Cool in a desiccator for thirty minutes, and weigh as rapidly as possible. Continue igniting and weighing until two consecutive weighings do not differ by more than 0.3 mg. Calculate and report the percentage of calcium oxide thus obtained.

**Determination of Magnesium.** Acidify the filtrate from the calcium with dilute hydrochloric acid, evaporate to a volume of

200 cc. and cool. Add 25 cc. of the sodium phosphate reagent, then slowly introduce 25 cc. of dilute ammonium hydroxide, which should impart a strong odor of ammonia to the solution, and finally set aside for at least ten hours. Decant off the clear solution through a 9-cm. filter and discard the filtrate; place the beaker containing the main part of the precipitate under the filter and pour through it the smallest possible amount of hydrochloric acid needed to dissolve the precipitate on the filter and in the beaker. Some 5 cc. of the reagent diluted to 25 cc. should suffice; then wash the filter free of soluble compounds.

Next add to the solution in the beaker, which should have a volume of about 50 cc., 5 cc. of sodium phosphate solution and then sufficient ammonium hydroxide to make it distinctly alkaline and give an excess of 20 cc. Stir the mixture occasionally during an interval of twenty minutes, then filter on a 9-cm. filter and wash with dilute ammonium hydroxide as in the analysis of magnesium sulfate.

Separate the precipitate and weigh as in the analysis of magnesium sulfate. Calculate the percentage of magnesium oxide present.

**Determination of Hygroscopic Water.** Weigh out 0.8 gram of the sample in 10-cc. platinum or porcelain crucible, which is provided with a cover. Place in a drying oven and heat to a temperature of  $105^{\circ}$  for an hour, and weigh accurately. Calculate the per cent of hygroscopic water from the loss in weight thus found.

**Determination of Loss on Ignition.** Place the crucible containing the residue from the previous determination on a wire triangle and heat over a Méker or Chaddock burner until the weight is constant, using all of the precautions used in the ignition of the calcium oxalate precipitate. Calculate the percentage loss and report as loss on ignition.

Finally recalculate all the percentages thus far obtained to show the composition of the water-free sample.

### III. Questions and Problems. Series 16

1. Are there any objections to precipitating iron (a) with potassium hydroxide instead of with ammonium hydroxide, (b) in the ferrous instead of the ferric

condition, (c) from a solution of the sulfate or nitrate rather than the chloride?

2. What experiments might be made for the purpose of showing that aluminum hydroxide forms a hydrosol? What reagents might be used to prevent the formation of a hydrosol in the quantitative determination of aluminum?

3. Complete precipitation of manganese as dioxide by means of bromine is prevented by the presence of ammonium salts and nitrogen gas is liberated. Give the reactions between bromine and (a) manganous ion, (b) ammonium ion. What factors determine which of the two possible reactions should take place if the amount of bromine added is not sufficient to react with both ions?

4. Give the reaction by which manganous ion is oxidized to permanganate ion by sodium bismuthate assuming the active component of the latter is bismuth dioxide. Why is chloride ion avoided in making this test?

5. If the sample of limestone used for this analysis contained small amounts of strontium or barium carbonates, in what manner would the determinations here outlined have been affected?

6. Indicate the equilibria which are of importance when the occlusion of magnesium by calcium is reduced by the presence of hydrochloric acid.

7. Suppose a sample of limestone contained, in addition to 5 per cent of the insoluble silicates, only calcium carbonate and magnesium carbonate, and suppose further that the loss on ignition amounted to 45 per cent, what percentages of calcium and magnesium were present?

8. A certain sample of limestone is known to contain a rather large percentage of insoluble matter. Would you expect that strong ignition of the sample before decomposing it with acids would have any effect on the final results?

## CHAPTER XX

### DETERMINATION OF SULFUR IN IRON PYRITES

#### I. Facts upon Which the Determination is Based

**Composition of Iron Pyrites.** This mineral, represented by the symbol  $\text{FeS}_2$ , is usually associated with other minerals representing simple or double sulfides of copper, zinc, lead, and arsenic, and with quartz and various insoluble silicates. Samples which have been exposed to moist air for some time frequently contain small amounts of sulfates owing to the slow oxidation of the sulfur. The mineral is used for the production of sulfur dioxide in the manufacture of sulfuric acid, as the sulfur present in this form is rapidly burned to sulfur dioxide in a properly constructed furnace. It will be assumed that the sample used for the analysis contains from 35 to 50 per cent of sulfur and only negligible amounts of lead and sulfates. It is also assumed that the sample has been crushed to pass a sixty-mesh sieve, thoroughly mixed, and dried.

**Oxidation of Sulfides.** The sulfur present as a sulfide of normal composition may be determined directly by a number of gravimetric or volumetric methods, but the sulfur of pyrites is in a peculiar form. Its valence must be represented by  $-1$  if that of the iron is assumed to be  $+2$ . If iron pyrites is treated with hydrochloric or sulfuric acid of moderate concentration, it is slowly acted upon and yields hydrogen sulfide and free sulfur. If treated with strong nitric acid it is acted upon rapidly and yields sulfate ion and free sulfur. It is not possible therefore to use the methods employed for the determination of sulfur in easily soluble sulfides of normal composition for the determination of sulfur in iron pyrites, and it is customary to oxidize both the sulfur atoms present to sulfate ion and separate the latter as barium sulfate.

There are two general types of procedure used for the oxidation. In the wet method the sample is treated with a mixture of a mineral acid and a strong oxidizing agent, such as a soluble nitrate or chlorate or bromine. In the dry method it is fused with a mixture of sodium carbonate and either sodium peroxide or potassium nitrate. The fusion process necessitates the use of a large amount of sodium carbonate and hence the solution from which the sulfate ion must be separated contains a large concentration of sodium salts. Since these cause rather large errors from occlusion and are not easily eliminated, this procedure is less satisfactory than the wet method.

Most samples of iron pyrites can be completely and rapidly oxidized by means of a mixture of three volumes of concentrated nitric acid and one of hydrochloric acid. With certain samples, especially if the temperature of the mixture is not allowed to rise too high, which causes the decomposition to take place too rapidly, there may separate small amounts of free sulfur, which is more difficult to oxidize than the sulfur of the iron pyrites. It can usually be oxidized by the addition of a few drops of liquid bromine which combines directly with free sulfur. The escape of small amounts of hydrogen sulfide during the oxidation is to be avoided. This loss of hydrogen sulfide can be prevented if the decomposition is made to take place in a sealed glass tube, but there is little danger of appreciable losses if the decomposition is made in a beaker whose diameter is so related to the volume of oxidizing solution used that the escaping gases must pass through a layer of solution at least 1 cm. thick.

**Reduction of Iron before Precipitation.** The solution which results from the oxidation must contain all the iron present in the ferric form, and as noted on page 137, low results are obtained if barium sulfate is separated from solutions containing ferric iron. Removal of the iron by precipitation with ammonium hydroxide is somewhat troublesome and necessarily adds to the solution ammonium ion, which also leads to slightly low results (see page 141). If nitrate ion has been already eliminated, the addition of less than 0.5 gram of finely powdered aluminum to the solution rapidly reduces the iron, and the effect of the added aluminum ion upon the precipitation of barium sulfate is negligible.

**Standardization of Procedure.** This determination has been made the subject of a large number of careful investigations<sup>1</sup> and most of the difficulties and sources of error are known. There is, however, no agreement as to the best method of avoiding the difficulties, and many procedures, the details of which depend in some measure upon the degree of accuracy required, are in use.

It is not difficult to formulate a procedure which yields a solution similar in composition to that used for the determination of sulfate ion in soluble sulfates and to make the entire scheme of analysis fit into the requirements named for this analysis. The use of half a gram of sample yields from 1.3 to 1.8 grams of barium sulfate and unless extreme care has been used in crushing and mixing the sample this is as small an amount as is desirable to use. The excess of nitrate ion used in oxidizing the sulfur is easily expelled by evaporating with hydrochloric acid (see page 41). Although the solution contains free sulfuric acid, there is no danger of expelling any of it if care is taken to evaporate below 250° C. that is, by evaporation on a steam bath. The concentration of chloride ion, and also of hydrogen ion in the solution, need not greatly exceed that present in the solution used for the standard procedure if the volume is kept small until the iron has been reduced. In the first analysis of a sample of unknown composition, it is necessary to calculate the amount of barium chloride needed on the assumption that the sample contains 50 per cent of sulfur, and to add this amount plus the usual excess of 2 cc. Owing to the greater amount of precipitate separated and the large amount of chloride ion present, it is desirable to make the volume of the solution 400 cc. before precipitation.

## II. Detailed Outline of Procedure

**Oxidation of Sample.** Weigh out a half gram of sample into a narrow 100-cc. beaker, cover with a watch glass, and introduce 25 cc. of a mixture composed of 11-cc. of concentrated nitric and 10 cc. of concentrated hydrochloric acid. If action does not

<sup>1</sup> See especially Hinze and Webber, *Zeit. für analytische Chemie*, 45, 31 (1906); Allen and Johnston, *Jour. of Ind. and Eng. Chem.*, 2, 196 (1910); Allen and Bishop, *Eighth Int. Congress of Applied Chem.*, Vol. I, 33 (1913).



begin to take place within a few minutes, warm gently; if at any time it becomes violent, restrain it by cooling the beaker with a stream of tap water. When brown fumes are no longer given off, and when the residue contains no particles of brassy-yellow color, it may be assumed that the decomposition is complete. If the sample is decomposed too rapidly, yellowish or greenish-yellow particles, which consist for the most part of free sulfur, will float in or on the solution. The oxidation should then be completed by adding a few drops of liquid bromine (not bromine water) and placing on the steam bath.

**Displacement of Nitric Acid.** Remove the cover from the beaker, rinse off with a stream from the wash bottle, and evaporate to dryness on the steam bath. Add 10 cc. of dilute hydrochloric acid and again evaporate to dryness. Next add 5 cc. of dilute hydrochloric acid, and, after it has stood for a few minutes, add 25 cc. of water. Finally digest until the acid ferric sulfate, which dissolves very slowly and can be recognized by the peculiar silky sheen which it imparts to the solution, has been dissolved and only sand and insoluble silicates remain.

**Reduction of Ferric Iron.** Cover the beaker and introduce about 0.3 gram of finely powdered aluminum, then warm and stir vigorously. This should cause some evolution of hydrogen and a gradual disappearance of the yellow color of the ferric ion. As soon as the solution is colorless dilute to 50 cc., filter on a 9-cm. filter into a 500-cc. beaker, and wash very carefully till the filter paper is shown to be free from ferric ion.

**Precipitation and Separation of Barium Sulfate.** Dilute to 400 cc., heat to the boiling point, slowly add the proper amount of barium chloride reagent, and allow to stand for at least an hour. Filter on a 11-cm. filter, wash till the washings give no test for chloride ion, then dry and ignite the precipitate as described on page 154. Calculate and report the percentage of sulfur present.

### III. Additional Facts on the Determination

Duplicate determinations by the method here outlined should not differ by more than 0.2 per cent and should give very nearly

the true percentage of sulfide sulfur plus that present as soluble sulfate. Samples which contain large amounts of lead or calcium, or even small amounts of barium or strontium, may not give the total percentage of sulfur present owing to the separation with the gangue matter of insoluble sulfates. With samples of unknown composition the gangue matter should therefore be examined for sulfate sulfur. Further, the commercial value of the sample depends upon the sulfur which is liberated as sulfur di- or trioxide when burned in a properly constructed furnace. Since this treatment has little or no effect upon these sulfates an accurate evaluation of the sample would also require determination of the soluble sulfates present, that is, leaching of the sample with water and determination of sulfate ion in the resulting solution.

### Questions and Problems. Series 17

1. Write the balanced equation representing the action of nitric acid on iron pyrites, assuming  $\text{Fe}^{+++}$ ,  $\text{SO}_4^{--}$ ,  $\text{NO}$ , and  $\text{H}_2\text{O}$  are the only products formed.

2. Calculate the concentrations of all the ions in the solution from which barium sulfate is precipitated, assuming that we start with 0.5 gram of a sample containing 40 per cent sulfur as  $\text{FeS}_2$ , that none of the 5 cc. of 6 N HCl added after the final evaporation is evaporated, that all the 0.3 gram of aluminum added is dissolved, and that the final volume is 400 cc.

3. Show what becomes of (a) zinc sulfide, (b) lead sulfide, (c) arsenious sulfide present in a sample which is analyzed by this process.

4. Explain why (a) nitric acid is eliminated before the iron is reduced, (b) the volume of the solution is kept small till nitric acid is eliminated and ferric ion reduced, (c) a mixture of nitric acid and hydrochloric acid is a better oxidizing agent than nitric acid alone, (d) how bromine acts as an oxidizing agent.

5. Why is metallic aluminum used to reduce the iron rather than (a) hydrogen sulfide, (b) sulfur dioxide, (c) zinc?

6. What would you expect to take place when iron pyrites is heated in (a) a good supply of air, (b) an atmosphere of carbon dioxide?

## CHAPTER XXI

### DETERMINATION OF SILICA IN HORNBLENDE

#### I. Facts upon Which the Determination is Based

**Classes of Silicates.** Analysts distinguish between two classes of substances which contain silica, namely those which can be decomposed by treatment with mineral acids and those which require treatment with other reagents. The former includes most of the rock-forming minerals; the latter includes certain naturally occurring silicates, of which the zeolites are the most important, and a large number of artificial products, especially Portland cement and certain slags, which are formed in the smelting of ores of iron, copper and lead. Slags in which the sum of the basic constituents, that is, oxides of calcium, iron and magnesium, is large as compared with the acidic constituents, that is the oxides of silicon and titanium, and which have been "chilled," that is, rapidly cooled from the molten state, are most easily decomposed. Many slags belong to the insoluble group of silicates.

**Decomposition of Insoluble Silicates.** Insoluble silicates must be decomposed by treatment with hydrofluoric acid, or changed into silicates of the soluble class by fusion with certain fluxes. If the hydrofluoric acid method is employed the decomposition must be carried out in vessels of platinum, and since the silicon present forms volatile silicon fluoride, it cannot be determined unless the apparatus is of such a form that the liberated gas may be absorbed in an appropriate reagent. Such an apparatus is too costly for general use.

The transformation into silicates of the soluble class can be effected by fusion with any strongly basic reagent, such as the hydroxides, oxides or carbonates of metals of the sodium and calcium groups. Such fusions must necessarily be made in vessels

free from silicon; a platinum crucible is to be preferred but one of silver or nickel is sometimes used. A mixture of four parts sodium and five parts potassium carbonates, which melts at  $685^{\circ}$  and has very little action on platinum, has many advantages. The alkaline hydroxides melt at much lower temperatures, and react with silicates more rapidly than the carbonates, but their action on platinum is also greater. The hydroxides possess the additional advantage of not liberating carbon dioxide during the decomposition, which may lead to mechanical losses. Both groups of reagents, especially the hydroxides, may be expected to contain small amounts of silica and alumina, and the percentages present should be determined and corrected for.

**The Dehydration of Silicic Acid.** When a soluble silicate is treated with an excess of hydrochloric acid, free silicic acid and the chlorides of all the metals present are formed. If the acid used is dilute and the temperature is kept low the silicic acid may remain in solution, but if these conditions are not complied with most of it separates as a gelatinous colloid, which is extremely difficult to filter. When the mixture is evaporated to dryness the silicic acid gradually loses water and assumes a fine, powdery form.

Experience shows that complete conversion of the silicic acid into an insoluble form is not easily affected. Some chemists dry the residue from evaporation at a temperature of  $120^{\circ}$  for a half hour or more, but this results in the formation of compounds of iron and alumina which are very difficult to dissolve, others dry at  $105^{\circ}$  or evaporate to complete dryness on the water bath several times. Two evaporations with an intermediate filtration of the dehydrated silicic acid are more effective than two successive evaporations, but even when this method is adopted small amounts of silica may be left in the solution. In dissolving the soluble salts from the residue left after evaporation either cold water or hot dilute acid should be used; if hot water alone is employed the iron and aluminum present may form insoluble basic salts. Even when the mixture is evaporated on the water bath only, the silica obtained may contain small amounts of iron and aluminum, but the error resulting from this is largely counter-balanced by the error from incomplete dehydration. Where the

highest degree of accuracy is demanded it becomes necessary to volatilize the silica in the precipitate by treating it with hydrofluoric and sulfuric acids in a platinum crucible, and determining the impurities, representing iron and aluminum oxides, remaining; also, to separate the silica, which has remained in the solution, but is subsequently precipitated with the iron and alumina. These refinements are not usually considered necessary in commercial work.

**The Ignition of Silica Precipitates.** The ignition of a silica precipitate requires extreme care owing to its fine powdery nature. If the paper filter used is heated too rapidly, and especially if it catches fire and burns at the mouth of the crucible, appreciable amounts of the precipitate may be carried off by the air currents formed. There is no danger of reducing or otherwise changing the composition of the precipitate, but long-continued ignition at the highest temperature readily attainable with a burner is necessary to completely convert the precipitate into the dioxide.

**Composition of Hornblende.** The hornblendes include a large number of species of minerals whose main components are metasilicates of calcium, magnesium, ferrous iron and aluminum. They may be considered to be solid solutions of the compounds named and therefore show large variations in the percentages of the component elements. Like all the naturally occurring silicates they may be expected to contain small amounts of many additional basic elements, especially manganese, chromium, ferric iron, sodium and potassium. The large percentage of magnesium frequently found in these silicates makes them more difficult to decompose by fusion than silicates which contain calcium, aluminum and the alkali metals only. The magnesium increases the temperature needed for fusion and makes it difficult to insure perfect interaction between the reagents concerned.

## II. Outline of Method of Procedure

**Selection and Preparation of the Sample.** Carefully select from the roughly crushed sample about 3 grams of the pure mineral. Place 0.5-gram portions at a time in a clean agate mortar and grind each portion until the resulting powder tends to form

a compact thin layer on the side of the mortar and no longer feels gritty when rubbed between the fingers. Place a perfectly clean 100-mesh sieve over a piece of glazed paper, brush the powdered mineral into the sieve and tap it until all the fine powder has passed through it. Return the powder left on the sieve to the mortar and continue grinding and sifting until all of it has passed through the sieve. Finally transfer the powdered mineral into a clean, dry, well-stoppered weighing tube.

**Fusion.** Weigh out in a platinum crucible of at least 10-cc. capacity about 4 grams of pure sodium carbonate. Weigh the tube containing the silicate and pour from it into the crucible about 0.7 gram of the sample and again weigh accurately. Thoroughly mix the silicate with the fusion mixture by the use of a platinum spatula or a stirring rod which has a carefully rounded end, then brush from the latter any of the adhering mixture and tap the crucible till the mixture is well settled.

Place the crucible on a triangle and heat it with a low flame for about five minutes, then gradually increase the temperature until the mass begins to fuse and keep at this point until carbon dioxide is no longer evolved. The crucible should be kept covered to avoid loss from spattering and the temperature must be carefully controlled or the mixture may boil over. The entire fusion should require from twenty minutes to half an hour and should finally yield a quiescent mass of perfectly sintered but only partially fused material.

Remove the crucible from the triangle by means of a pair of forceps while still hot, and by carefully tipping and rotating the crucible cause the contents to solidify as a layer around its inner surface. When cold place the crucible on its side in the bottom of a 5-inch casserole, add 50 cc. of water, warm and stir until the fused mass is disintegrated and falls out of the crucible, then remove the crucible from the dish with the aid of a glass rod and wash both inner and outer surfaces thoroughly. Cover the dish with a watch glass and gradually introduce 20 cc. of hydrochloric acid. The dish should now contain only gelatinous silicic acid and a clear yellow solution. If sandy or gritty particles are present the decomposition is probably incomplete and a second sample must be fused. Sometimes the precipitated silica has a

reddish color owing to the presence of difficultly soluble iron compounds, which usually dissolve on digestion.

**Separation of Silica.** Place the dish on the steam bath and evaporate to complete dryness, that is, till powdery dry. The evaporation may be made more rapidly by heating on a sand bath, or over a gauze placed some distance above the flame of the burner if the precipitate is kept in constant motion with a stirring rod. Moisten the residue with about 10 cc. of concentrated hydrochloric acid and then add 1 cc. of nitric acid and 50 cc. of water, and digest on the steam bath until all basic salts have been decomposed and white silicic acid only remains.

Filter through a 9-cm. filter and transfer the precipitate to the filter, then wash twice with 10-cc. portions of cold water. Next transfer the filtrate and washings which may still contain small amounts of silicic acid to the casserole previously used, evaporate the mixture to complete dryness on the steam bath and keep the dry residue on the bath one half hour longer. While the solution in the dish is evaporating continue to wash the silica precipitate until the washings are shown to be free from chlorine, receiving the washings in a clean 300-cc. beaker.

Treat the residue from the second evaporation with 20 cc. of dilute hydrochloric acid and digest until all basic salts have been decomposed, add 50 cc. of water and then filter through a fresh 9-cm. filter, receiving the filtrate in the beaker containing the washings from the first silica precipitate. Next rub the entire inner surface of the dish with a rubber-tipped rod until the adhering precipitate has been loosened, and rinse into the filter; finally wash the latter until free from soluble salts.

Place the two still moist filters in a weighed crucible and heat cautiously over a wire gauze until combustible gases are no longer given off, then place the crucible over a wire triangle and gradually increase the temperature until the paper is entirely consumed; finally ignite over a blast lamp, or Méker burner for at least twenty minutes and weigh. Repeat the ignition till the weighings are practically constant.

**Determination of Silica in Reagents.** Weigh out 10 grams of the sodium carbonate used into a casserole, cover with a watch glass and cautiously introduce sufficient dilute hydrochloric

acid to decompose it. Evaporate to complete dryness and separate the silica as in the analysis. Calculate the weight of silica in the weight of fusion mixture used in the analysis and subtract from the weight of precipitate found. Report the corrected per cent of silica present.

### III. Questions and Problems. Series 18

1. Give the reactions which take place when orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) is decomposed (a) by treatment with hydrofluoric acid, (b) by fusion with sodium carbonate, (c) by fusion with sodium hydroxide.

2. What might take place if a silicate which was associated with silver chloride was fused with sodium carbonate in a platinum crucible?

3. When an alloy of iron and silicon is dissolved in hydrochloric acid and the mixture evaporated to dryness, the silicon separates as silicon dioxide. Give the reactions concerned.

4. What elements are most closely related to silicon in their analytical behavior?

5. A certain mineral is found to contain the following percentages:  $\text{SiO}_2$ , 55.64;  $\text{Al}_2\text{O}_3$ , 15.11;  $\text{Fe}_2\text{O}_3$ , 3.08;  $\text{FeO}$ , 6.85;  $\text{MgO}$ , 7.80;  $\text{CaO}$ , 2.40;  $\text{Na}_2\text{O}$ , 9.34;  $\text{MnO}$ , 0.56. Is it an ortho- or a meta-silicate?



## SECTION IV

### SOLUTION AND EXTRACTION PROCESSES

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#### CHAPTER XXII

#### GENERAL FEATURES OF SOLUTION AND EXTRACTION PROCESSES

**Solution Processes Which Depend upon the Physical Action of the Solvent.** These processes depend upon the differential action of liquids on mixtures composed of two or more solids. The simplest possible example is one in which the mixture consists of two distinct solid phases, each phase representing a single component, one of which is much more soluble in some particular liquid than the other. If the difference in solubility is sufficiently large, and if the mixture is so finely divided that every particle of the more soluble constituent is exposed to the action of the solvent, treatment of the mixture with a sufficient amount of the solvent at once yields a liquid phase which contains all of the more soluble component, and a residual solid phase composed of the less soluble component. The action concerned is the converse of that of precipitation processes, but the rate at which equilibrium is attained when a liquid acts upon a solid is slower than when a precipitate is formed in a liquid, and although the theory of the two classes of methods is essentially the same, the methods by which they are carried out are decidedly different.

The ideal method of making such a separation would be to use only sufficient solvent to bring into solution all of the more soluble component, but such a method of procedure would not be practicable owing to the slowness with which solution of the last particles of the more soluble constituent is effected, and

the adherence of some of the liquid to the solid phase, which makes it necessary to wash the residue with further quantities of the solvent. The general theory of the method actually used in carrying out such processes is similar to that elaborated in Chapter XII for the washing of precipitates. The comparative rates at which the two components pass into solution, the effect of one component upon the solubility of the other, the size of the particles of which the mixture is composed, and the relative amounts of the two components, all affect the accuracy and efficiency of such processes. An ideally perfected method for making a separation of this kind would prescribe the weight of the mixture to be used, the composition and amount of the solvent to be used for each treatment, the number of treatments, and the length of time allowed for each treatment. These details are best determined empirically, that is, by quantitative experiments with mixtures of known composition; in many of the processes largely used these details have only been determined very roughly.

In discussing the theory of this class of methods it is assumed that the two components of the mixture exist as distinct and separate solid phases. Some doubt should always be entertained as to whether the method can be successfully applied to the separation of a mixture of isomorphous substances which has separated from a solution, or has resulted from the solidification of a molten magma; that is, wherever the presence of solid solutions is possible. A solvent which readily dissolves one of the two components of a solid solution will often, especially where the less soluble component is present in relatively small amounts, readily disintegrate and decompose such a mixture, but not in all cases.

This class of methods is of especial use in the separation of those elements all of whose compounds are largely soluble in aqueous solvents, and which, therefore, cannot be separated by the use of precipitation methods. In using them it is often necessary to convert the substance to be separated into those particular compounds which possess the necessary differences in solubility in some particular solvent.

**Solution Processes which Depend upon the Chemical Action of the Solvent.** Processes in which the action of the solvent

is chemical as well as physical are also extensively used. In all such cases two sets of equilibria must be considered. The equilibrium resulting from the contact of solvent and one of the solids must result in the formation of a single liquid phase, that is, must involve a change from heterogeneous to homogeneous equilibrium; that resulting from contact of the solvent with the other solid must involve maintenance of the original condition.

As in the case of processes in which the action of the solvent is purely physical the formation of solid solutions often makes it impossible to effect separations which could otherwise be easily made. The chemical as well as the physical properties of solid solutions are specific properties of the mixture, and vary with the comparative amounts of the two components actually present. Thus, although metallic silver is readily changed into a solution of silver nitrate by treatment with a dilute solution of nitric acid, it is not possible to separate silver from gold in an alloy which contains more than 30 per cent of gold because the two metals form a continuous series of solid solutions.

**Extraction Processes.** Further difficulties are encountered in applying this class of methods to the analysis of certain classes of materials such as plant and animal tissues. In such substances the soluble constituent may be diffused through or surrounded by cell walls, which act as semi-permeable membranes and prevent diffusion of the solvent. The difficulty can be overcome to some extent by mechanical disintegration and crushing of the sample, but even where the sample is reduced to a very fine powder it is often necessary to treat it with the solvent for many hours. To successfully carry out such a separation by supporting the mixture on a filter and washing with the solvent is impracticable, as it necessitates the use of very large amounts of the solvent, which is often an expensive reagent, and demands a large amount of time, and care from the analyst. It is then necessary to "extract" the substance in an apparatus of especial construction, which is known as an "extraction apparatus."

Extraction methods are of especial importance in the analysis of mixtures containing organic compounds for, owing to the low temperatures employed in carrying on the process, and the slight activity of the solvents which are most frequently

used, the probability of decomposing these compounds is reduced to a minimum. They are universally used in the analysis of substances of animal or vegetable origin, of all classes of explosives, and of asphalt paving materials.

**Apparatus for Continuous Extraction.** The conditions necessary for the rapid and complete extraction of any solid substance are most readily and effectively maintained by boiling the solvent in a small flask attached to an inverted condenser so arranged that the condensed solvent is made to fall into, and drip through a filter containing the substance to be extracted. An apparatus of this kind is represented in Fig. 41. It consists of a wide-mouthed flask *A* of about 125-cc. capacity, which contains the boiling solvent; an extraction tube *B*, which supports the "extraction shell" *C* containing the sample; and the condenser *D*. The vapor of the boiling solvent passes through the side tube *E* into the condenser, and after condensation falls into the extraction shell, where it comes into contact with the sample, passes through the shell, and falls back into the flask. Fresh portions of the pure warm solvent are thus continuously brought into contact with and made to pass through the shell and its contents, and gradually wash out those constituents which are soluble. As these are usually much less volatile than the solvents used they accumulate in the flask in the form of a solution, whose concentration increases as the process of extraction progresses.

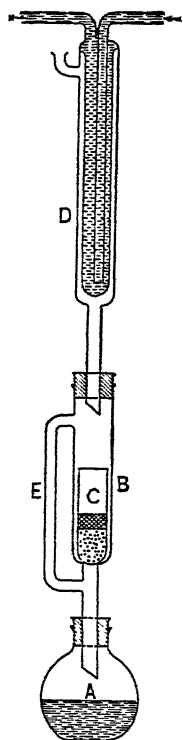


Fig. 41.—Continuous extraction apparatus.

A more compact, and in some respects more desirable, apparatus is the one devised by Wiley, which is represented in Fig. 42. The substance to be extracted is here placed in a Gooch crucible *C*, which is suspended from the very efficient metallic condenser *B*; both crucible and condenser are contained in the tube *A*, which holds the boiling solvent. Both figures represent forms of extraction apparatus in which the distilled and con-

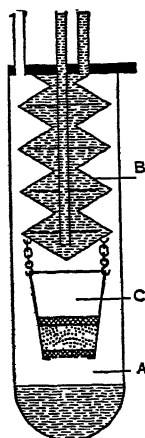


Fig. 42.—Wiley extraction apparatus.

densed solvent is made to leach the sample continuously and are therefore designated as "continuous."

**Apparatus for Intermittent Extraction.** Another type of apparatus, of which there are also many forms, acts intermittently rather than continuously. It is represented by the Soxhlet apparatus shown in Fig. 43 and differs from the apparatus already described in the form of the extraction tube. This is closed at the point *A*, but is provided with a side tube *B* through which the vaporized solvent passes into the condenser, and a siphon tube *C* through which the solution, which accumulates in the extraction tube, runs back into the flask as soon as it reaches the level *D*. The action of this type of apparatus is distinguished

by the fact that a large volume of the solvent remains in contact with the sample for a relatively long time; since, however, there is little circulation, that portion of the solvent in immediate contact with the sample soon attains a fairly large degree of concentration with respect to the soluble compound, which delays further solution. By using the method of reasoning already employed in discussing the theory of washing precipitates it is easy to show that the continuous type of apparatus should be more efficient than the intermittent, and a comparison of the efficiency of the two types under similar conditions confirms the accuracy of this conclusion; furthermore, the amount of solvent required to operate the continuous type of apparatus is much less than that required for the intermittent.

**Construction of Joints to Apparatus.** The solvents which are most extensively used are alcohol, ethyl ether, petroleum spirit, chloroform, carbon disulphide and carbon tetrachloride. All of these are extremely volatile, and all except chloroform

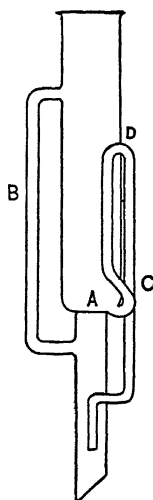


Fig. 43.—Soxhlet extraction tube.

and carbon tetrachloride are extremely inflammable. It is essential, therefore, that all joints of the apparatus should be tight, and that the condensation of the vaporized solvent should be as perfect as possible. Rubber dissolves to some extent in all of the solvents named except alcohol, and such media as wax or paraffin, which are sometimes used to remedy the deficiencies of cork stoppers, are also dissolved appreciably by these solvents. It is desirable, therefore, to use an apparatus, like the Wiley apparatus already described, which has no joints, or one which is made entirely of glass; if the latter alternative is adopted the ground-glass joints which become necessary must be very carefully made, and they are both expensive and easily broken.

Still another alternative involves the use of an apparatus, such as the Knorr apparatus represented in Fig. 44 or the Ames apparatus represented in Fig. 45, in which the only joint which is exposed to the action of the solvent is provided with a "mercury seal." In both forms the flask in which the solvent is made to boil is provided with a groove into which the tube *B* fits loosely, the intervening space being filled with sufficient mercury to prevent the escape of any of the vaporized solvent.

Where these more elaborate and therefore more expensive types of apparatus are not available, recourse must be had to simpler forms, in which the joints are made by means of cork stoppers. These can usually be made to give tight joints if corks of good quality and large size are chosen, boiled in water for an hour, and while still hot and plastic forced into the opening to be closed, and then allowed to dry in this position; they should be bored to fit the necessary connections when dry and cold.

**Methods of Heating the Apparatus During Extraction.** Since the rate at which the soluble constituent is leached out depends

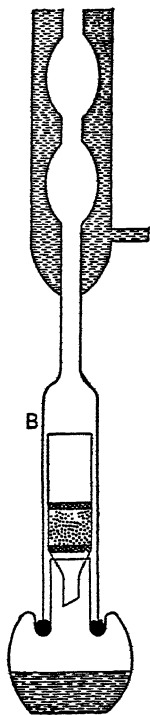


Fig. 44.—Knorr extraction apparatus.

upon the rate at which the solvent circulates through the extraction shell, it is desirable to heat the solvent by means of a device which causes it to boil vigorously and steadily, that is, without danger of boiling over. Direct heating of the flask with a flame is always to be avoided, since it is hard to regulate the rate of boiling, and if the flask cracks or if the joints of the apparatus

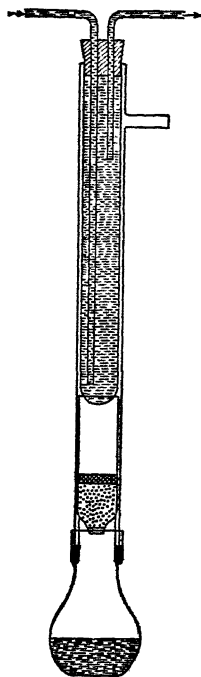


Fig. 45.—Ames extraction apparatus.

are not tight the flame may set fire to the escaping solvent. The use of a water bath is more satisfactory but has some disadvantages. An electric hot plate or an air bath heated by a current passing through resistance wires or incandescent lamps is to be preferred to all other devices, since the danger from fire is reduced to a minimum and any desired temperature can be maintained by the use of proper resistances in the circuit.

#### Determination of the Separated Constituent.

The weight of the constituent dissolved from the sample can be determined from the difference between the weight of the sample and that of the solid residue left, or if the substance extracted is not appreciably volatile, the solvent can be distilled off from the solution and the desired weight determined directly. Where the former method is used difficulties may arise from the hygroscopic character of the residue or of the extraction shell used. The alternative method of procedure is always to be preferred unless the dissolved constituent is so volatile that appreciable amounts of it are carried over with the

solvent during the distillation.

**Multiple Extraction Apparatus.** Although the actual labor involved in making a determination by an extraction method is small, it is often necessary to extract a sample for several hours, and where a large number of such determinations have to be made it becomes almost imperative to operate a number of such apparatus simultaneously. Many forms of multiple

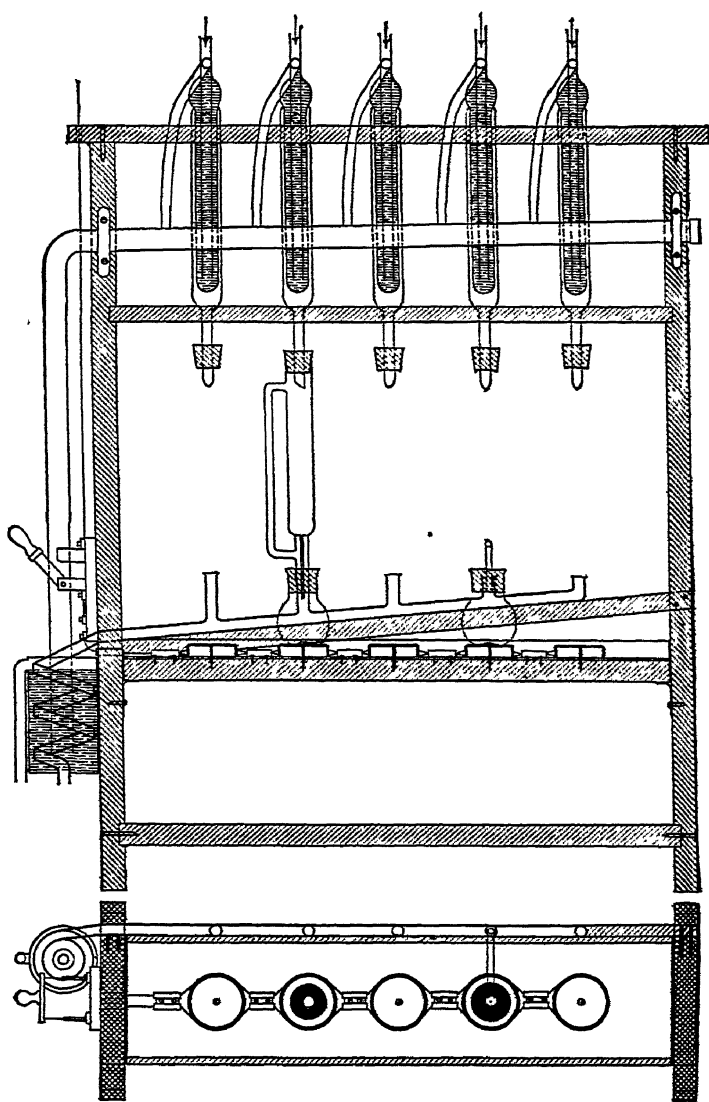


Fig. 46.—Plan of a multiple extraction apparatus.



extraction apparatus in which a series of extraction units are supported on a common frame, and supplied with a common source of heat and condenser water are in use. An apparatus<sup>1</sup> consisting of five such units is represented in Fig. 46; this apparatus is also provided with a common device for the distillation and condensation of the solvent after the extraction has been completed.

The heating device here used consists of five electrically heated iron plates supported on a wooden base, but separated from it by a sheet of asbestos. The edge of each plate is surrounded by a strip of mica, which prevents the plate from short-circuiting the resistance wire by which it is heated, but does not prevent the transfer of heat to it. A nichrome wire 0.01 mm. in diameter passes through a series of cleats fastened to the bed and makes three complete turns around, and in close contact with, the edge of each of the five plates; this wire is connected directly with the terminals of a 110-volt alternating current by means of a switch. The wire offers a resistance of 75 ohms and consumes 1.5 amperes.

The condenser used during distillation consists of a worm of block tin tubing supported in and surrounded by a cylindrical copper vessel through which the waste water from the other series of condensers can be made to flow. One end of the worm passes through the bottom of the copper vessel, the other is prolonged and supported in a position slightly inclined to the horizontal on a strip of wood fastened to the back of the frame of the apparatus. The prolonged end is provided with five vertical branches placed at points opposite to the centers of the five heating plates. Connection can be easily established between any of the flasks resting on one of the plates and the lateral opposite it by means of a glass tube.

<sup>1</sup> Further details concerning the construction of this apparatus will be found in the *Jour. of Ind. and Eng. Chem.*, 4, 302 (1912).

## CHAPTER XXIII

### DETERMINATION OF POTASSIUM IN COMMERCIAL POTASSIUM SULFATE

#### I. Facts upon Which the Method is Based

**Composition of Samples.** This salt is largely used as a fertilizer and its commercial value is proportional to the percentage of potassium, usually reported as potassium oxide, which it contains. In addition to sulfate of potassium it contains sulfates and chlorides of sodium and magnesium.

**Choice of Method.** With the exception of a complex nitrite, which has the formula  $\text{KNa}_2\text{Co}(\text{NO}_2)_6$ , the compounds of potassium are too soluble in water to make it possible to determine this element by a precipitation process. The two methods, which have been most largely used up to the present time, involve conversion of the element into the perchlorate ( $\text{KClO}_4$ ) or chloroplatinate ( $\text{K}_2\text{PtCl}_6$ ) in a solid form, and elimination of all of the other salts present in the mixture thus obtained, by treating it with certain solvents, that is, by methods which are essentially solution processes. Of the three methods suggested the chloroplatinate method is to be preferred, especially where the amount of potassium present is small, on account of the large molecular weight of the compound finally separated and weighed, and also because the details of the method have been carefully worked out. Although the reagent used is very expensive the platinum can be easily recovered after use and reconverted into a further quantity of reagent.

**Formation of Potassium Chloroplatinate.** Solutions containing mixtures of potassium and sodium chlorides are completely converted into  $\text{K}_2\text{PtCl}_6$  and  $\text{Na}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  respectively, by evaporating almost to dryness with the theoretically required

amount of chloroplatinic acid. The potassium salt separates in well-formed octahedra belonging to the regular system; the sodium salt in plates belonging to the triclinic system. The two compounds do not form double compounds nor solid solutions with each other, nor with the chlorides of sodium, potassium, platinum or magnesium. The sulfate of potassium is readily changed into the chloroplatinate by the same treatment, but the sulfate of sodium is not so readily changed into the corresponding sodium compound. The reagent used for this purpose should be of known strength and of high concentration if economy in its use and in the time needed for the evaporation is to be attained. A solution which contains  $\text{H}_2\text{PtCl}_6$  equivalent to 0.1 gram of Pt per cubic centimeter is a suitable one to employ.

**Properties of Potassium Chloroplatinate.** At a temperature of  $20^\circ$  one part of this compound requires about 98 parts of water, or 26,400 of 80 per cent alcohol, or 42,600 of absolute alcohol for complete solution. Ammonium chloroplatinate, which may be formed by the absorption of ammonium hydroxide from the atmosphere of the laboratory, is also extremely insoluble in these reagents. Both the hydrated and anhydrous sodium chloroplatinate and chloroplatinic acid are readily soluble in 80 per cent alcohol, but the chlorides and sulfates of sodium, potassium and magnesium are but slightly soluble in this reagent.

When made to separate by the evaporation of moderately dilute solutions, potassium chloroplatinate is coarsely crystalline and does not contain either combined or occluded water. It can be dried at a temperature of  $135^\circ$  without danger of decomposition or volatilization; at higher temperatures it is slowly decomposed into potassium chloride, chlorine and metallic platinum; it is not appreciably hygroscopic.

**Development of the Lindo-Gladding Method.** In 1881 Lindo <sup>1</sup> showed that potassium could be determined in solutions containing chlorides of sodium and potassium by evaporating to dryness with sufficient chloroplatinic acid to convert both elements into chloroplatinates, leaching out the sodium salt with strong alcohol and weighing the residual potassium salt. The method

<sup>1</sup> Chemical News, 44, 77, 86, 87, 97, 129 (1881), Bull. 7, Division of Chem., U. S. Dept of Agriculture.

could not be used when sulfate ions were present owing to the insolubility of sodium sulfate in alcohol and although this ion could be removed by the use of barium chloride, and the excess of barium added could be removed by the use of ammonium carbonate this procedure greatly increased the difficulties of the method. Gladding modified the method by washing the mixture first obtained with sufficient alcohol to remove all of the sodium chloroplatinate and chloroplatinic acid, and then with sufficient ammonium chloride solution to remove the sodium sulfate. This modification made it possible to apply the method to substances containing organic matter and ammonium salts, for, by evaporating with a slight excess of sulfuric acid and igniting gently, both classes of substances could be expelled without loss of potassium. It also made it possible to apply the method to substances containing magnesium salts, as they are readily dissolved by solutions of ammonium chloride. The slight solubility of potassium chloroplatinate in the solution of ammonium chloride used was reduced to zero by saturating it with potassium chloroplatinate before use.

The method has been investigated by the Official Association of Agricultural Chemists and the exact details of the best method of procedure as applied to different classes of substances formulated. The outline given below is the official method<sup>1</sup> as applied to commercial potassium sulfate.

## II. Outline of Method of Procedure

**Preparation of Solution.** Weigh out 10 grams of the sample into a 500-cc. beaker, add 300 cc. of water, boil for a few minutes, then transfer to a 500-cc. graduated flask. Allow to cool, dilute to exactly 500 cc., mix thoroughly, filter about 300 cc. through a dry filter and preserve in a stoppered flask.

**Separation of Potassium.** Measure out 25 cc. of the solution by means of a pipette, add an equal volume of water, acidify with a few drops of hydrochloric acid, add 10 cc. of chloroplatinic acid (1 cc. = 0.1 gram Pt) and evaporate on the water bath almost to dryness. Remove from the bath and add 25 cc. of 80

<sup>1</sup> Bull. 107, Bureau of Chemistry, U. S. Dept. of Agriculture.

per cent alcohol, stir the mixture with a rod and break up any large masses, and after about five minutes decant off the clear liquid through a weighed Gooch or alundum filtering crucible. Treat the residue with three 10-cc. portions of 80 per cent alcohol, stirring the mixture for several minutes after each addition and decanting as before. The last addition should remain colorless; if it acquires even a faint yellow color continue the washing. Finally transfer the residue to the filter by means of a stream of 80 per cent alcohol from a wash bottle.

Wash the residue on the filter five times with 10-cc. portions of ammonium chloride wash solution,<sup>1</sup> then with three 10-cc. portions of 80 per cent alcohol. Dry the crucible for a half hour at 100° and weigh accurately. Calculate and report the percentage of potassium as potassium oxide present. Save both the precipitate in the crucible and the filtrate and washings for the recovery of the platinum present.

### III. Questions and Problems. Series 19

1. How much larger percentage error is involved in determining potassium when separated as potassium perchlorate than when separated as potassium chloroplatinate, assuming that the sample contained 2 per cent of potassium, that one-half gram was used and that an error of 0.1 mg. was made in weighing both compounds?

Ans. 0.12.

2. What is the maximum error from solubility in the determination of potassium oxide in a substance which contains 20 per cent, assuming that all of the details outlined above are followed?

Ans. 0.15.

3. Why is it desirable to evaporate on a *water bath* after adding the chloroplatinic acid? Why is it necessary to wash out all sodium chloroplatinate and chloroplatinic acid before washing with ammonium chloride? What might happen if the mixture was heated after alcohol was added? Why is it desirable to avoid changes in temperature while washing with the ammonium chloride solution?

4. What modification of the method outlined would be necessary if the sodium and potassium were present as nitrates or phosphates respectively?

<sup>1</sup> Prepared by dissolving 100 grams of ammonium chloride in 500 cc. of water, adding from 5 to 10 grams of pulverized potassium chloroplatinate and shaking at intervals for from six to eight hours. Allow this mixture to settle over night, then filter. The residue may be used for the preparation of more solution.

5. Outline a method for reconvertng the platinum saved from the determination into chlor-platinic acid.

6. The potassium and sodium in a 0.5 gram sample of potassium sulfate are converted into a mixture of the chlorides of sodium and potassium, which is found to weigh 0.35 gram; the potassium is then separated as potassium chloroplatinate, which is found to weigh 0.65 gram; what percentages of potassium and sodium oxides are present? *Ans.* 25.20  $K_2O$  and 14.30  $Na_2O$ .

7. Outline all the transformations necessary to carry out the determinations represented in the last problem.

## CHAPTER XXIV

### DETERMINATION OF CRUDE FAT IN PEANUTS

#### I. Facts upon Which the Determination is Based

**Chemical Nature of Fats and Oils.** In the analysis of foods the different constituents are classified and determined with reference to the function they perform in the nutrition of the animal body. One of the most important of these groups consists of fats and oils; it includes a very large number of organic compounds, which are analogous to inorganic salts, in that they represent combinations of certain organic acids and glycerine, which acts as a trivalent base. The most important are olein, palmitin and stearine, which represent normal salts of oleic ( $C_{17}H_{33}COOH$ ), palmitic ( $C_{15}H_{31}COOH$ ) and stearic ( $C_{17}H_{35}COOH$ ) acids, respectively. These compounds are not appreciably hygroscopic and do not absorb oxygen from the air, but the "drying oils," which are obtained when flax and certain other seeds are extracted, contain linoleic acid ( $C_{17}H_{31}COOH$ ), and since this compound rapidly absorbs oxygen from the air such oils are difficult to weigh accurately.

**Meaning of "Crude Fat."** All of the compounds referred to above are distinguished by their extreme insolubility in water, and very slight solubility in alcohol; also by the readiness with which they are dissolved by ethyl ether, petroleum spirit, carbon disulfide and carbon tetrachloride. The remaining constituents of most food materials are not appreciably soluble in the four solvents last named. Many classes of food materials contain small amounts of other substances such as wax, resin, chlorophyll and various coloring matters, which are also more or less soluble in these solvents, especially in ethyl ether. Long established custom has led to the use of dry ethyl ether for the determina-

tion of this group of food constituents. Since the results obtained by extracting a material with ether may include small amounts of substances other than fat the result should always be designated as "crude fat" or "ether extract."

**Purification of Ether.** Unless especially purified ether contains both alcohol and water, and is then capable of dissolving appreciable amounts of certain sugars and other compounds which are not true fats. The alcohol can be removed by shaking the solvent with water and allowing the mixture to stand until it separates into two layers. The upper ethereal layer is then removed and the large amount of water which it contains separated by adding solid calcium chloride, and allowing the resulting aqueous solution of calcium chloride to separate out; the residual ether is then made anhydrous by adding metallic sodium and distilling. The purified solvent should boil at  $35^{\circ}$ . From 35 to 50 cc. are needed for each extraction where the continuous type of apparatus is used, but nearly 25 cc., which can be again used without further treatment, should be recovered when it is distilled from the fat.

**Composition of Peanuts.** The seeds of the peanut contain from 40 to 50 per cent of substances soluble in ether, nearly all of which are true fats. At least 80 per cent of the ether-soluble substances is triolein and the remainder is made up of the glycerides of stearic, arachidic ( $C_{19}H_{39}COOH$ ) and lignoceric ( $C_{23}H_{47}COOH$ ) acids. None of these substances absorbs oxygen from the air at an appreciable rate and hence no difficulty is experienced in weighing the crude fat separated directly. On the other hand, the cellulose-containing residue, which remains after extraction, is appreciably hygroscopic.

**Conditions Necessary for Complete Extraction.** Ether penetrates cellular tissue even when dry but slowly, and still more slowly when the tissue is moist. If the sample contains much moisture it is slowly taken up by the dry ether used, and gradually accumulates in the ethereal solution. Since the water cannot be easily distilled off from the crude fat without using an undesirably high temperature an appreciable error may result if the sample is not dried before it is extracted.

The large amount and liquid character of the fat present makes it impossible to grind these seeds in a mill, or to pass the ground



pulp through a sieve. They can be crushed to a sticky mass in an agate mortar, but this will still contain small lumps unless great care is taken. The pulp can be completely dehydrated by drying for an hour at  $105^{\circ}$  and the residue can usually be completely extracted in three hours if the apparatus used is efficient, and if not more than 3 grams of sample is used. Time can be saved and greater accuracy assured if the extraction is continued for an hour, the almost completely extracted residue ground very fine and the extraction continued for an hour longer.

## II. Outline of the Method of Procedure

**Preparation of the Sample.** Select eight or ten nuts of average size and maturity and remove the husks and the brown skin which envelops the seeds by means of a thin-bladed knife. Place the seeds on a porcelain plate or watch glass and cut into thin slices with a knife, then place in an agate mortar and crush to a pulpy mass till free from lumps. Weigh out 3 grams of the sample into a closed, dry weighing bottle, place in a drying oven and keep at a temperature of  $105^{\circ}$  for an hour. Determine the loss in weight which results and calculate the percentage of water present.

**The Extraction.** Transfer the dried sample to a paper or alundum extraction shell and cover with a half-inch layer of cotton wool, which has been previously extracted with ether to remove the small amount of fat which it usually contains. Place the shell in an extraction tube similar to *C* of Fig. 41 or Fig. 43. Weigh accurately a clean, dry fat-flask of 125-cc. capacity, add 35 cc. of pure dry ethyl ether and connect with the extraction tube by means of an accurately fitting cork stopper. Connect the extraction tube with the vertical condenser as shown in Fig. 46 and adjust the cork stoppers so that the flask rests directly on one of the iron heating plates, then start the water running through the condenser. Close the switch which operates the heating device and after the ether begins to boil reduce the rate at which it boils, if this seems to be necessary, by interposing a thin sheet of asbestos over the heating plate. Adjust the end of the condenser so that all of the condensed ether falls inside the extrac-

tion shell and allow the process of extraction to continue for three hours.

**Weighing the Crude Fat.** Disconnect the extraction tube and flask from the condenser, remove to some distance from any source of heat and allow to drain for about five minutes. Disconnect the flask from the extraction tube and then connect the flask with one of the branches of the block-tin condenser tube. Place a receiving flask under the other end of the tin condenser tube and allow the ether to distill over until only about 2 cc. of yellow or brown oil remains. Then remove the flask and place in a water-jacketed oven, heat the water to boiling and keep at this temperature for an hour. Draw a current of dry air through the flask by means of an aspirator until the residue gives no odor of ether. Allow the flask to cool and weigh accurately. Calculate the percentage of crude fat in the dried sample and in the original selected nuts.

## SECTION V

### PARTITION PROCESSES

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#### CHAPTER XXV

#### GENERAL FEATURES OF PARTITION PROCESSES

**Conjugate Liquids.** The solubility of certain pairs of liquids with respect to each other is unlimited, that is, an infinite number of homogeneous solutions representing every possible ratio of the two constituents can be prepared. With other pairs of liquids the possibilities are limited; either liquid may become saturated with respect to the other, and if a greater amount of one liquid than is needed to saturate the other is added, a second liquid phase separates. If small amounts of water are successively added to ethyl ether and the mixture is shaken after each addition, a single phase containing a relatively large percentage of ether is first obtained, but when the amount of water added exceeds 3 per cent by volume of the ether a second phase containing about 90 per cent of water separates. The addition of further quantities of water does not change the composition of the ether phase, but increases the amount of water-rich phase at the expense of the ether-rich phase, and if a sufficient amount is added will cause the entire disappearance of the latter. The addition of still further quantities of water merely increases the percentage of water in the water-rich phase.

Certain pairs of liquids, such as kerosene and water, are so slightly soluble in each other that the addition of a very small amount of either liquid to the other at once produces two liquid phases, whose composition is practically the same as that of the pure components. Any pair of liquids which continue to exist

as independent liquid phases after being shaken together and allowed to stand until equilibrium has been attained, are called "conjugate liquids." The mutual solubility of two liquids which form a conjugate pair of liquid phases is affected by changes in temperature. Increasing the temperature usually increases their mutual solubility and may cause them to become miscible in any proportions, that is, may result in the disappearance of one of the two phases.

**The Distribution Coefficient.** When a small amount of a third substance is added to a system consisting of two conjugate liquids, the whole shaken for some time and allowed to stand until perfect equilibrium has resulted, the added substance, or a certain part of it distributes itself between the two phases. The ratio of the concentration of the dissolved substance in one phase to the concentration in the other is a definite quantity, which is independent of the magnitude of the concentrations concerned, provided the dissolved substance does not dissociate and does not form molecular aggregates. This ratio can be easily determined experimentally and is known as the "distribution coefficient." Its value is affected to some extent by temperature changes. If the two liquids are but slightly soluble in each other, and if the added substance is much more soluble in one than in the other the value of the distribution coefficient will be either very large or very small, depending upon which of the two solutions concerned is taken as the standard of comparison. If, however, the two liquids possess a more nearly equal solvent power for the added substance, or if the two liquids dissolve one another to a large extent, so that the composition of the two resulting liquid phases does not greatly differ, the value of the distribution coefficient becomes more nearly equal to unity.

**The Separation of Two Liquid Phases.** The two liquid phases which make up a conjugate system can be mechanically separated by a variety of devices. The simplest method is to insert a pipette or a tube, similar to the one shown in Fig. 47, into the mixture till its end is slightly above the plane separating the two layers, to draw the upper layer into the tube by suction, and transfer the liquid to another vessel. The separation thus effected is always imperfect as it is impossible to remove all of the upper layer

without also removing some of the lower layer, but this error is comparatively small if the area of the containing vessel at the point of contact of the two layers is small.

A much more satisfactory device is a "separatory funnel," one of the many forms of which is represented in Fig. 48. This is provided with a glass stopper and a side tube, which can be closed with the finger or a good cork, so that the two liquid phases can be shaken together vigorously. The lower of the two resulting layers can then be allowed to drain into another vessel by opening the glass stopcock at the bottom of the funnel. The inaccuracy



Fig. 47.—Separatory pipette.

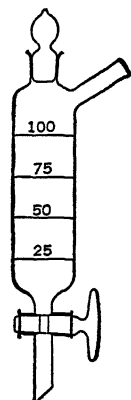


Fig. 48.—Separatory funnel.

of the separations made with such a device is due almost wholly to the small volume of the heavier liquid which adheres to the inner surface of the tube below the stopcock; for this reason this tube should be made as short as possible and of such a diameter that capillarity does not prevent it from discharging readily after the stopcock has been closed.

Difficulties arise in the separation of two liquid phases when one or both liquids show a tendency to "emulsify," that is, to form an intimate mixture composed of small bubbles of the two liquids, which do not segregate except after very long standing. Instances occasionally arise in which this difficulty is sufficient to make the process concerned an impracticable one. The presence of any

finely divided solid matter always retards and may prevent an entirely satisfactory segregation of the two liquids.

**General Theory of Partition Processes.** Iodine is much more soluble in liquid carbon tetrachloride than in water and these two liquids are but slightly soluble in each other. As a consequence of these facts the distribution coefficient of iodine between the two liquid phases which result when carbon tetrachloride is added to an aqueous solution of iodine, has at ordinary temperatures the value 85. This means that every unit volume of the carbon tetrachloride-rich phase will contain eighty-five times as much iodine as each unit volume of the water-rich phase. The total amount of iodine separated from an aqueous solution by this treatment would also depend on the volume of the aqueous, as compared with that of the carbon tetrachloride phase. Suppose, for example, it is assumed that the aqueous solution has a volume of 100 cc. and contained 0.2 gram of iodine, that 50 cc. of carbon tetrachloride is added, and that the changes in volume which result after equilibrium has been established are insignificant. If  $x$  represents the weight of iodine in the resulting aqueous phase  $0.2 - x$  must represent the weight of iodine in the carbon tetrachloride phase. The distribution coefficient would require that

$$\frac{x}{100} : \frac{0.2 - x}{50} :: 1 : 85.$$

When this expression is solved for  $x$  the latter is found to have the value 0.0046, that is, the weight of iodine in the aqueous solution is reduced to 4.6 mg. by this treatment.

If now the carbon tetrachloride solution is separated from the mixture, and the residual aqueous solution is again treated with 50 cc. of carbon tetrachloride a further quantity of iodine will be taken up by the latter. If  $y$  represents the weight of iodine left in the aqueous solution after this second treatment, the distribution coefficient would require that

$$\frac{y}{100} : \frac{0.0046 - y}{50} :: 1 : 85.$$

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The value of  $y$  calculated from the expression is found to be 0.0001016.

The calculation shows then that practically all of the iodine can be separated from the aqueous solution by two treatments with 50-cc. portions of carbon tetrachloride. It can be readily shown that the use of only 75 cc. of this liquid in three 25-cc. portions would have left only 0.018 mg. of iodine in the aqueous solution and in general, several treatments with small amounts of carbon tetrachloride is more efficient and economical than fewer treatments with larger amounts. It is also obvious that the smaller the volume of the solution from which the substance is to be determined is separated, the greater the efficiency of the process.

In general, the theory of partition processes shows a close analogy to that already developed in discussing the washing of precipitates, but unlike the latter it does not involve the use of assumptions which are never actually realized. Further emphasis should be laid, however, on the qualification already noted, namely, that the value of the distribution coefficient may change with varying concentration. This may result from the effect of varying concentration upon the degree of ionization or of hydration, or upon the nature of the substances actually present in the solution concerned.

## CHAPTER XXVI

### DETERMINATION OF NICKEL IN NICKEL STEEL

#### I. Facts upon Which the Determination is Based

**Composition of the Sample.** Alloys of nickel and iron, which contain from 1 to 14 per cent of nickel are frequently used for structural purposes where extreme hardness and toughness are demanded, and where the importance of these factors warrants the extra cost of such an alloy. They usually contain small amounts, up to 1 per cent, of combined carbon, very small amounts of silicon, sulfur and phosphorus and sometimes appreciable amounts of manganese and copper.

Although nickel hydroxide is readily soluble in an excess of ammonium hydroxide, this reagent cannot be used to effect a quantitative separation of nickel from iron unless the process is repeated several times, or unless the percentage of iron present is very small, owing to the occlusion of nickel by ferric hydroxide.

An accurate separation of nickel in the presence of iron can be made by use of the reagent known as dimethyl glyoxime, and this reagent is largely used for such separations. There are, however, many instances in which it becomes desirable to first separate iron from solutions containing a number of metallic ions and the partition process first devised by Roth is extremely convenient in such analyses.

**Theory of the Separation.** Anhydrous ferric chloride, unlike the chlorides of aluminum, nickel, cobalt, chromium, manganese, zinc and copper, is readily soluble in ethyl ether. If, however, ethyl ether is added to an aqueous solution of ferric chloride very little iron is taken up by the resulting ethereal solution unless a large concentration of hydrochloric acid or some soluble chloride is also present. It is probable that only unionized ferric chloride



is appreciably soluble in ether, and that the element cannot be separated by the use of ethyl ether unless the ionization of the ferric chloride is repressed by the addition of hydrochloric acid. The best results are obtained when the iron solution treated contains from 20 to 25 per cent of this acid.

The value of the distribution coefficient which is concerned here is not constant, but varies with the temperature and the concentration of both acid and ferric chloride in the aqueous solution; under favorable conditions it may attain a value of 100. The values for the distribution coefficients of the chlorides of the metals named above, except possibly copper, are represented by extremely small fractions.

**Conditions Necessary for the Separation.** The rate at which iron was removed from an aqueous solution, which had a volume of 20 cc. and contained in addition to 20 per cent of hydrochloric acid 0.2054 gram of iron as ferric sulfate, by successive treatments with 25-cc. portions of ether, is shown in the following results:

Iron removed by first treatment.....	0.1964 gram
Iron removed by second treatment.....	0.0075 gram
Iron removed by third treatment.....	0.0016 gram
Iron removed by fourth treatment.....	0.0007 gram
Iron removed by fifth treatment.....	0.0002 gram

Since ferrous salts are not appreciably soluble in ether all of the iron must be kept in the ferric condition during the separation. As ether reduces ferric salts appreciably at a temperature slightly above the normal the mixture must be kept cold. It is further necessary to keep the concentration of all anions except chloride ion low; if such anions are present they may keep some of the iron in such a form that it is not easily taken up by the ether.

**Determination of the Separated Iron.** Most of the ethyl ether present in the ethereal solution can be recovered for subsequent separations by distilling in a suitable apparatus; were it not so the cost of the method would often be prohibitive. The last traces can be driven off by evaporating in an open vessel; the iron which has been reduced during the distillation and evaporation must be oxidized before it is precipitated.

**Determination of the Separated Nickel.** The decomposition voltage of the nickel ion is about 0.22 volt higher than that of the

hydrogen ion. It can be rapidly and completely separated in a dense form from a neutral solution of the double oxalate, or from solutions of the sulfate to which a large excess of ammonium hydroxide has been added. In the presence of the nitrate ion a small amount of nickel oxide, which is not readily redissolved, may separate at the anode. The precipitated metal is not dissolved appreciably by the ammoniacal solution and it is not easily oxidized.

## II. Outline of Method of Procedure

**Preparation of the Solution.** Weigh out 2 grams of the sample, which should be in the form of drillings or shavings, into a 300-cc. beaker, add 20 cc. of dilute hydrochloric acid, 5 of dilute nitric acid, cover with a watch glass and warm the mixture until the alloy is dissolved. Remove the watch glass cover and evaporate the solution cautiously to avoid loss from spattering until a thick syrupy liquid or solid residue remains. Add 10 cc. of concentrated hydrochloric acid to the residue and evaporate as before; finally dissolve the residue in 10 cc. of dilute hydrochloric acid, dilute to 20 cc., filter off the small residue of silica and carbon on a 7-cm. filter and wash free from soluble salts, using the smallest necessary amount of cold wash water.

**Separation of the Iron.** Concentrate the filtrate to a volume of 10 cc., allow to cool and then transfer the solution to a 100-cc. separatory funnel with the aid of 10 cc. of dilute hydrochloric acid and 50 cc. of ether. Place both glass and cork stoppers in the funnel, cool the latter under a stream of water from the tap, shake cautiously once and release the excess of pressure created in the funnel by cautiously opening the cork stopper. Replace the cork stopper, again cool the funnel and shake vigorously for about three minutes. Support the funnel in a vertical position by means of a clamp and allow it to stand until the plane separating the two liquid phases is clearly defined. Remove the cork stopper and cause the aqueous phase to drain into the beaker previously used, allowing sufficient time to permit the aqueous phase to flow down the inner surface of the funnel and several drops of the ethereal phase to flow through the stopcock; then rinse off the lower end of the funnel with 2 or 3 cc. of water. These precau-

tions become necessary for the purpose of rinsing every drop of the aqueous phase out of the funnel before attempting to remove the ethereal phase. Allow the ethereal phase to flow into a 200-cc. Erlenmeyer flask, rinse off the inner and outer surfaces of the tube below the stopcock with 3 to 5 cc. of water, then close the stopcock and set the flask aside. Transfer the aqueous solution in the beaker to the funnel with the aid of 25 cc. of ether and again mix and separate the ethereal layer. Connect the Erlenmeyer flask containing the combined ether extracts with a condenser and carefully distill off the ether, which can be used for subsequent determinations.

**Separation of Last Traces of Iron.** Add cautiously 5 cc. of concentrated sulfuric acid to the aqueous solution and warm gently until the ether present is expelled, then heat nearly to the boiling point and evaporate the solution until fumes of sulfur trioxide appear; next add 50 cc. of water, and digest until soluble salts are dissolved, then add 5 cc. of hydrogen peroxide to oxidize any iron which may have been reduced by the ether, heat to the boiling point and add an excess of ammonium hydroxide, that is, sufficient to impart a strong odor to the solution. Keep the solution at or near the boiling point for a few minutes, then filter off the precipitated iron and manganese on a 7-cm. filter and wash with the smallest necessary amount of hot water.

**Determination of Nickel.** Ignite and weigh accurately a clean platinum electrode, preferably of gauze. Place the electrode and a platinum spiral in the nickel solution, add 20 cc. of dilute ammonium hydroxide and make the proper connections with the terminals of a storage battery. If a gauze electrode has been prepared use a current of 1 ampere and allow the action to continue for at least fifteen minutes after the solution has become colorless. If a foil electrode has been prepared, it will be preferable to use a current of one-half ampere only. Remove the cathode, wash in alcohol, dry at 100° and weigh. Calculate the percentage of nickel present. Remove the nickel from the cathode by allowing it to stand in a cylinder of strong nitric acid for twenty minutes and rinse off the acid with water.

## III. Questions and Problems. Series 20

1. Calculate the values of the distribution coefficient for iron in the ethereal as compared with the aqueous phase at different concentrations from the data given on page 256. *Ans.* 17.46 and 4.

2. Discuss the factors to which the changes in the values of this distribution coefficient are due.

3. A solution, which has a volume of 100 cc. and contains 0.4 gram of mercuric bromide is treated successively with 20-cc. portions of benzene; if the distribution coefficient, that is, the ratio of mercuric bromide in water to mercuric bromide in benzene, has the value 0.88, how many treatments are needed to reduce the amount of  $\text{HgBr}_2$  to 0.1 mg.? *Ans.* 41.

4. Write out a probable reaction for the reduction of ferric chloride by ether.

5. Suggest a probable effect of the presence of alcohol in the ether used for this separation.

6. What objections are there to precipitating the iron by means of ammonium hydroxide without previous oxidation?

7. Explain how nickel might separate at the anode during electrolysis and how nitrate ion could favor the separation.

8. Would you expect the electrolytic determination of nickel to be affected by the presence of cobalt, copper, zinc, lead or silver?

## SECTION VI

### GENERAL FEATURES OF VOLUMETRIC PROCESSES

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#### CHAPTER XXVII

#### THEORY OF VOLUMETRIC PROCESSES

**Fundamental Definitions.** Volumetric analysis is that branch of quantitative analysis in which the amount of an element or compound, which is present in the substance submitted to analysis, is calculated from the volume of some reagent of known strength that is found to be necessary to complete a reaction with the element or compound being determined. A reagent especially prepared for making such a determination is known as a "standard solution." The value of this solution may be expressed either in terms of the number of grams of reagent actually present in a unit volume, or in terms of the number of grams of any substance with which the reagent in one unit volume reacts. The process of determining the volume of standard solution necessary to complete a reaction with a solution of the substance which is being analyzed, and, in general, the process of comparing the relative strengths of two solutions which react with each other chemically, is designated as "titrating."

The essential difference between gravimetric and volumetric processes consists in the substitution of a measurement of a standard solution for a determination of the weight of a precipitate, or of some product which is separated from the substance being analyzed. Since volumetric processes necessarily involve calculating the magnitude of a weight which corresponds to the weight of precipitate or other product separated in a gravimetric

process, they are virtually indirect methods of carrying out gravimetric processes.

**Reactions Suitable for Volumetric Processes.** Volumetric processes are usually based upon definite chemical reactions, but only a limited number of reactions can be used as the basis of such processes. All of them assume that the reaction concerned is complete when equivalent amounts of the reacting substances are present in the reacting mixture. This is a theoretical ideal which is never exactly realized. There are, however, a number of reactions which involve the formation of insoluble or slightly ionized substances, which are so nearly complete that they can be used for such determinations without appreciable error. Many of the reactions used in gravimetric processes, which are made complete by using a large excess of either reagent, are not available for volumetric determinations. Such reactions should be, and usually are practically instantaneous. It is possible to use certain slow reactions by the method of "back titration." In employing this method a slight excess of the standard solution is added and the excess added is then titrated with a second standard solution, which is capable of reacting completely and instantaneously with the standard solution first employed. If the volumetric relation between the two standard solutions has been previously determined, the proper correction for the excess of standard solution first added is easily made.

A second requirement, which reduces still further the number of reactions which can be used for volumetric determinations, is that there must be some means of determining the point at which an equivalent amount of standard solution has been added. As this point is approached in making the titration, certain of the physical and chemical properties of the solution change very rapidly. In some cases there is a marked change in the color or the electrical conductivity of the mixture; in others a precipitate may begin to form or may cease forming; in still others the addition of another reagent, that is, an "indicator," causes a decided color change. The point at which a sufficient amount of standard solution has been added to make these changes recognizable is known as the "apparent end point" of the titration. The point at which an equivalent amount of the standard solution

has been added is the stoichiometric end point or "true end point" of the process. The accuracy of the final result depends very largely upon the extent to which these points can be made to coincide.

**Effect of Varying Volume.** In order to get a clear idea of the factors which determine the accuracy of volumetric processes, it is necessary to ascertain the actual concentrations of the reagents used at the true end points, and also the rates at which these concentrations change as the true end points are approached or exceeded. These values can be easily calculated for simple ideal cases by making use of a few simplifying assumptions. It will be assumed first that 25 cc. of a 0.1 molal solution of  $A^+$  is titrated with a 0.1 molal solution of  $N^-$ , forming the precipitate  $AN$ , whose solubility product is  $1 \times 10^{-8}$ . The values of  $(A^+)$  during the progress of the titration have been calculated by methods already described in Chapter X and are represented by means of Curve I of Fig. 49 in which the logarithm of  $(A^+)$  is plotted on the vertical and the number of cubic centimeters added on the horizontal axis. The true end point of the process is reached when 25 cc. of the 0.1 molal solution of  $N^-$  has been added, and must be characterized by the fact that both  $(A^+)$  and  $(N^-)$  equal  $\sqrt{1 \times 10^{-8}}$  or  $1 \times 10^{-4}$ . The graph is almost symmetrical with respect to horizontal and vertical lines passing through this point and would be exactly so if the volume of the mixture had been constant. Graphs II and III represent the results of similar calculations in which the initial volumes are 75 and 175 cc. respectively. The value of  $(A^+)$  at the true end point is necessarily the same for all these graphs, but the rate at which  $(A^+)$  changes as reagent  $N^-$  is added is greater with the smaller volume throughout the entire course of the curves. This difference is greatly accentuated as the true end point is approached or exceeded, and within 0.1 cc. of the true end point Curve I is practically vertical.

The form of the titration curve has an important effect upon the accuracy of the process. A perfect process would require that the device used to determine the end point should show a recognizable change in the mixture titrated when  $(A^+) = 1 \times 10^{-4}$ , but

such devices are not easily found. The probability of finding a device which will show a change when  $(A^+)$  attains a value somewhere between  $8 \times 10^{-4}$  and  $2 \times 10^{-5}$  is fairly large. This would correspond uncertainty of 0.1 cc. or an error of one in 250 if the concentration changes were in agreement with those of Curve I, but to much larger errors if they are in agreement with

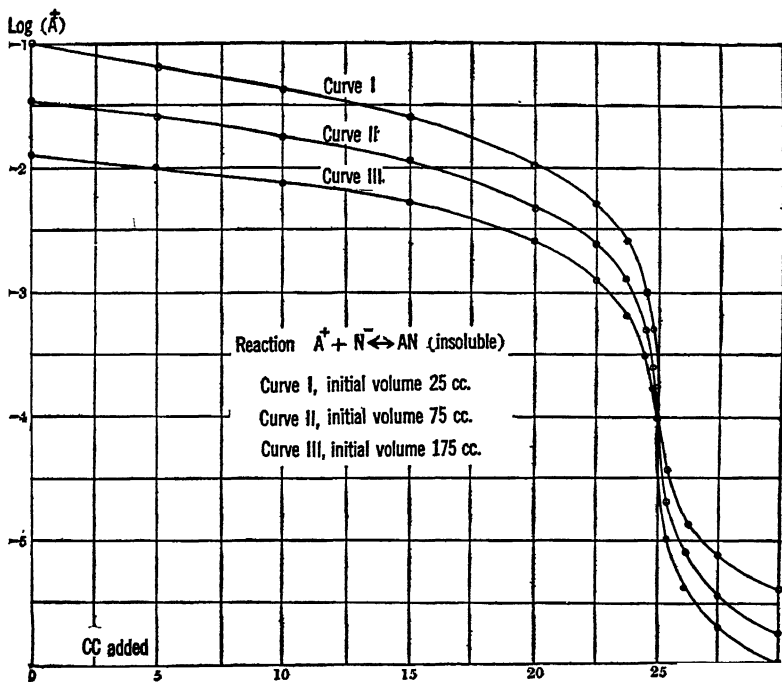


Fig. 49.—Titration curves showing changing concentration with varying initial volume.

Curves II or III. It is obvious therefore that the accuracy of the procedure increases with decreasing volume.

**Effect of Change of Equilibrium Constant.** The form of the titration curve must depend upon the value of the constant which determines the completeness of the reaction. The preceding discussion has shown that the accuracy of the process is



determined by the form of that portion of the titration curve immediately adjacent to the true end point, and, in studying the form of such curves in the future, only that portion which represents the interval corresponding to the addition of from 80 to 120 per cent of the theoretically required amount of titrating substance will be considered. Further, the effect of the volume change within this interval is relatively small, and such calcula-

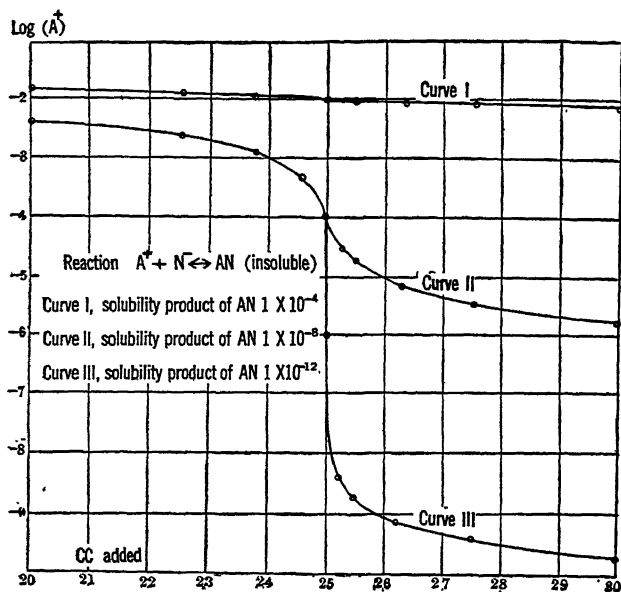


Fig. 50.—Titration curves showing changes in concentration with varying values of equilibrium constants.

tions will therefore be simplified by assuming that the volume is always the same as the volume at the true end point.

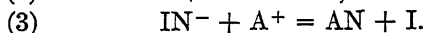
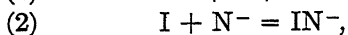
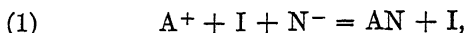
Curves representing the titration of 25-cc. portions of a 0.1 molal solution of  $A^+$  with 0.1 molal  $N^-$ , between the points at which 20 and 30 cc. have been added, assuming the volume of the mixture is always 100 cc., have been calculated for three different values of the solubility product of the compound AN. Graphs I, II, and III of Fig. 50 represent the results of these

calculations, in which it was assumed the solubility products were  $1 \times 10^{-4}$ ,  $1 \times 10^{-8}$  and  $1 \times 10^{-12}$  respectively. Graph II corresponds almost exactly to a portion of Graph II of Fig. 49, although the scale is different. The three curves show how large an effect the value of the solubility product has on the ratio of the change in  $(A^+)$  to the change in volume of the titrating solution. The rate of change, if the solubility product is  $1 \times 10^{-4}$ , is so small as to make it very doubtful whether an indicator which would make it possible to obtain an even approximately correct result could be found. The probability of finding a suitable indicator is greatly increased if the solubility product has the value  $1 \times 10^{-8}$ , and still more if its value is  $1 \times 10^{-12}$ . Decreasing the value of the solubility product also decreases the value of  $(A^+)$  at the true end points to  $1 \times 10^{-4}$  and  $1 \times 10^{-6}$  respectively.

Calculation of the value of  $(A^+)$  at the true end point and of the rate of change in  $(A^+)$  during the titration are more complicated if the insoluble compound formed is represented by  $A_2N$  or  $AN_2$ . The value of  $(A^+)$  at the true end point for the former is represented by  $\sqrt[3]{\text{Sol. Prod. } A_2N \times 2}$  and for the latter by  $\sqrt[3]{\text{Sol. Prod. } AN_2 \div 4}$ . The form of the titration curves for such a process would show essentially the same features as the ones already discussed. The accuracy of the very large number of volumetric processes, based upon reactions which involve neutralization, displacement, oxidation, or complex formation, also depends in every case upon the form of the titration curve. Examples of such processes will be discussed in subsequent chapters.

**The General Theory of Indicators.** Although the end points of volumetric processes are sometimes ascertained by the measurement of certain physical properties, such as the conductance, or the ability of the mixture being titrated to generate an electromotive force, they are more frequently determined by the use of an indicator, that is, a reagent capable of giving a recognizable color change at or near the true end point of the process. The indicator used may react either with the substance being titrated or with the reagent used in making the titration. In the latter case the reactions concerned may be represented by the following

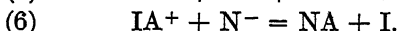
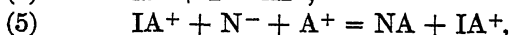
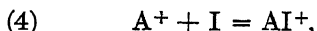
equations in which  $A^+$  represents the substance being titrated,  $N^-$  the titrating reagent, and  $I$  the indicator.



The appearance of the end point is here dependent upon the concentration of  $IN$ , which should remain equal to zero as long as  $(A^+)$  exceeds the value it should have at the true end point, but should increase rapidly as soon as  $(A^+)$  is less than that value. Practically all the  $A^+$  present should be changed to  $AN$  by reaction (1) before reaction (2) begins to take place, but (2) should take place promptly even when the concentration of  $N$  is small. It is further necessary that in case a small amount of  $IN$  is formed during the earlier stages of the titration, which may readily result from imperfect stirring and consequent accumulation of  $N^-$  in the upper layers of the solution,  $IN$  should react with  $A^+$  according to (3), thus preventing the appearance of false end points. Reaction (3) also expresses the ratio between the constants for (1) and (2).

The closeness of the agreement between the apparent and the true end points depends upon the values of the three equilibrium constants, and upon the concentration of the indicator used. Increasing the concentration of the indicator favors (2) and should lead to the appearance of an end point at an earlier stage in the titration. If the value of  $(A^+)$  at the true end point and the constant of reaction (2) are known, it is possible to calculate the concentration of indicator needed to make the apparent end point coincide with the true end point.

If the indicator reacts with the substance being titrated the series of reactions may be represented by



The appearance of the end point is then dependent upon the concentration of  $I$ , which should remain equal to zero as long as

(A<sup>+</sup>) exceeds the value it should have at the true end point, but should increase rapidly, owing to (6), as soon as it is less than this value. In this case also the accuracy of the process depends upon the values of three constants and the concentration of the indicator. Increasing (I) favors (4) and inhibits (6), and therefore delays the appearance of an end point.

A further factor relates to the nature and intensities of the colors of I and IN<sup>-</sup>. If either is colorless, it will not mask the color of the other, and the color of mixtures can be more correctly interpreted, even when large amounts of indicator are present, than if both are colored.

**Calculations in Volumetric Processes.** The general expression by means of which the results of volumetric determinations are calculated is:

$$\frac{\text{Vol. in cc. of Standard Sol. Used}}{\text{Weight of Sample Used}} \times (f) \times 100 = \text{Desired percentage.}$$

Here (f) is the weight of substance being determined which reacts with the reagent in 1 cc. of the standard solution used. The value of (f) can be calculated if the weight of reagent in 1 cc. of the standard solution and the equation representing the reaction are known.

It is advantageous to use a standard solution of such strength that (f) is a simple number. If, for example, (f) = 0.01 the desired percentage is the volume used divided by the weight of sample. Further, if the weight used is exactly 1 gram the desired percentage equals the volume used in making the titration. In order to make (f) equal 0.01, each cubic centimeter of solution must contain that amount of the active reagent which is chemically equivalent to 0.01 gram of the substance being determined. For example, if (f) = 0.01 gram of silver, and the reagent used is sodium chloride, 1 cc. of the solution must contain

$$.01 \times \frac{\text{Molecular weight of NaCl}}{\text{Atomic weight of Ag}}, \text{ or } .00542 \text{ gram of sodium chloride.}$$

Even if the process is a complicated one, that is, involves the use of a series of reactions, the standard solution used for the final

titration can be made to conform to the system, which can be conveniently designated as the "unitary system." If the standard solution is to be used for the determination of only one substance, the unitary system is the most convenient one to employ, but it is often desirable to use such solutions for the determination of a variety of substances, and when this is done, the calculations possess the desired simplicity of only one of the substances determined. For example, the sodium chloride solution, for which ( $f$ ) has the value 0.01 when used to determine silver, must have the value 0.01859 when used to determine mercury. It becomes necessary therefore, when this system is used, to prepare a solution for every substance determined. If many determinations of these substances are to be made, this may be a desirable thing to do, but frequently the extra labor involved in preparing and using the several different solutions more than offsets the gain in making the calculations.

**General Features of the Normal System.** When the standard solution is to be employed only occasionally, and for the determination of a variety of substances, it is preferable to make use of the so-called "normal system." The essential idea upon which this system is based is to use such concentrations that equal volumes contain equivalent amounts of the different reagents, and therefore that a mixture composed of equal volumes of any two such solutions which react with each other will not contain an excess of either reagent. In order to prepare such a series of solutions it is necessary that the standard volume, usually the liter, should contain amounts of the active reagents which bear a simple relation to the molecular weights of the compound concerned. The exact value of this relation may be conveniently estimated by comparing the chemical reactivity of the molecule with that of the hydrogen atom as a unit or standard. A normal solution is then defined as one which contains in a liter an amount of the active reagent chemically equivalent to 1.008 grams of hydrogen. Thus a normal solution of any acid, which contains a single replaceable hydrogen atom, and which is used in a reaction involving simple neutralization, must contain as many grams of that acid as there are units in its molecular weight. A normal solution of any base must be equivalent to a normal solution

of any acid; and hence, if the base contains a single hydroxyl group, the liter should contain an amount corresponding to its molecular weight expressed in grams; if it contains two hydroxyl groups it should contain one-half as many grams as there are units in its molecular weight.

Where the reagent is used in a reaction involving oxidation, reduction, or precipitation, exactly the same principle is used. In every case the oxidizing or reducing or replacing power of the molecule concerned, as compared with the oxidizing or reducing or replacing power of the hydrogen atom, determines the number by which the molecular weight must be divided to give the normal value. This number will be designated in this book as the "equivalency." Further details as to the method of computing the normal values of different reagents will be discussed as the different processes are described.

**Normal Values Dependent upon the Reaction Concerned.** It should be especially noted that the normal value of a substance may vary according to the type of reaction in which it is used. Thus the normal value of a solution of oxalic acid is determined by dividing its molecular weight by two, no matter whether used as a neutralizing, a reducing, or a precipitating agent; whereas the normal value of nitrous acid is the entire molecular weight when used as a neutralizing agent, but only is one-half its molecular weight when used as a reducing agent. Further than this, the same reagent may be used in two reactions which belong to the same type and have a different normal value for each. Thus phosphoric acid may be used in reactions in which it acts as a monovalent or a divalent acid; in the former case its normal value is the entire molecular weight, in the latter case it is one-half its molecular weight.

**Advantage of the Normal System.** Since a normal solution of any reagent must, according to definition, be chemically equivalent to a normal solution of any substance with which it reacts, every cubic centimeter of such a solution must be equivalent to as many grams of that substance as are present in a cubic centimeter of a normal solution of that substance. In other words, the value of 1 cc. of a standard solution, in terms of any substance with which it reacts, is determined by dividing the molecular

weight of the substance by one thousand times its equivalency. The general expression for the calculation of the results of a volumetric determination, where a normal solution is used, then becomes:

$$\frac{\text{Vol. of Solution Used}}{\text{Weight of Sample}} \times \frac{M \times 100}{1000 \times E} = \text{Desired percentage.}$$

Here  $M$  is the molecular weight,  $E$  is the equivalency of the compound determined, and the volume is expressed in cubic centimeters.

The advantage of the system is most striking where the process concerned is an indirect one, that is, where the method involves the use of a series of reactions. In such cases the stoichiometric method requires a separate calculation, involving one multiplication and division for every reaction concerned. By the use of the normal system it is possible from a mere inspection for the reactions concerned to calculate the value of the solution being used in terms of the substance being determined, by a single division. For example, potassium bitartrate may be determined by dissolving in water, neutralizing and precipitating as calcium tartrate, filtering off the precipitate and converting into calcium carbonate by igniting in an open crucible and titrating the resulting carbonate with standard hydrochloric acid. The reactions involved are:

- (1)  $\text{C}_4\text{H}_5\text{KO}_6 + \text{KOH} \rightarrow \text{C}_4\text{H}_4\text{K}_2\text{O}_6 + \text{H}_2\text{O}$ ,
- (2)  $\text{C}_4\text{H}_4\text{K}_2\text{O}_6 + \text{CaCl}_2 + 4 \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_4\text{CaO}_6 \cdot 4 \text{H}_2\text{O} + 2 \text{KCl}$ ,
- (3)  $2 \text{C}_4\text{H}_4\text{CaO}_6 \cdot 4 \text{H}_2\text{O} + 5 \text{O}_2 \rightarrow 2 \text{CaCO}_3 + 6 \text{CO}_2 + 12 \text{H}_2\text{O}$ ,
- (4)  $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ .

An inspection of these reactions shows that each molecule of bitartrate yields 1 of neutral tartrate, 1 molecule of neutral tartrate yields 1 of calcium tartrate, 1 of calcium tartrate yields 1 of calcium carbonate and 1 of calcium carbonate is equivalent to 2 of hydrochloric acid. Since the hydrochloric acid contains 1 replaceable hydrogen atom its equivalency is 1, hence the equiv-

alency of potassium bitrate, when determined by this process, is 2. The formula for the calculation of the result of the determination is:

$$\frac{\text{Vol. of Sol.}}{\text{Wt. of Sample}} \times \frac{\text{Mol. Wt. of } \text{C}_4\text{H KO}_6}{2 \times 1000} \times 100$$

= percentage of  $\text{C}_4\text{H}_5\text{KO}_6$ .

**Use of Solutions Which Bear a Simple Relation to Normal Strength.** Normal solutions are too concentrated to give the best results, and it is customary to prepare solutions which bear a simple relation to normal strength, that is, are either one-half, one-fifth or one-tenth normal. The results obtained by the use of such solutions are correctly calculated by introducing the factors one-half, one-fifth or one-tenth in the formula given above. Even where the solution has not been prepared to bear a simple relation to normal strength this method of calculation may still be employed to advantage. The relation of any solution to normal strength can be calculated by dividing the number of grams of active reagent in 1 cc. by the number of grams present in 1 cc. of normal solution of that reagent; or, it may be determined by dividing the number of grams of any substance with which 1 cc. reacts by the number of grams in 1 cc. of the normal solution of that substance. The resulting factor representing the exact relation of the solution to normal strength is then used in the above formula just as the simpler factors one-half, etc.

**Principle of Compensating Errors.** A principle which can be used to great advantage in volumetric processes is that of counteracting the errors involved in the actual determination by equal errors in the standardization of the solution used. Assuming that there is always a discrepancy between the true and the observed end point, it will generally be true that this discrepancy will be constant so long as the conditions remain constant. If the solution is standardized under the same conditions as those which must obtain in the actual determination, practically all the errors are eliminated, as the standard solution used becomes merely an instrument by means of which the strengths of two solutions of the same substance, one representing a known amount



of a pure compound and the other the solution of unknown concentration, are compared. Considered from this point of view it is always preferable to standardize the solution by comparing with a known weight of the substance being determined, and where it is possible to use the same solution for the determination of a number of substances, strict accuracy would demand that the solution be restandardized for every one of the substances for which it is to be used.

This principle would also justify basing volumetric processes on certain reactions which are not perfectly represented by any one single equation. It is to be expected that the ratio between the two substances which react with each other in such cases would vary greatly with varying temperature and concentrations, and volumetric processes based upon them would have to be carried out within a rather narrow range of these conditions.

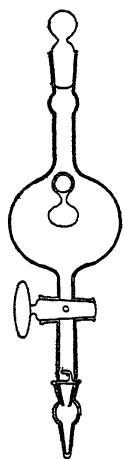


Fig. 51.—Weight burette.

**Titration by Weight.** It will be shown in the following chapter that although it is possible to devise methods by which the percentage error in the measurement of the solution used in making a titration can be made negligible, the devices usually employed are not accurate to 0.01 cc. and may cause rather large percentage errors. This error is much greater than that involved in weighing the sample, and in most cases exceeds the error in determining the end point of the process. There is no objection to weighing the standard solution used in making the titration provided a suitable container is available. One form of such a container is represented in Fig. 51. Its total weight when charged with 50 cc. of solution is about 80 grams and requires a balance capable of weighing such a load to within 0.01 gram. Obviously the solution used should also

be standardized in terms of grams of reagent present or grams of substance reacted upon per gram of solution. This procedure will always be found to be the more convenient one to use when a high degree of accuracy is demanded, or when the amount of solution used in making the titration is necessarily small.

## CHAPTER XXVIII

### MEASUREMENT OF SOLUTIONS IN VOLUMETRIC DETERMINATIONS

#### I. Factors Affecting Accuracy

**Forms of Volumetric Apparatus.** The accuracy of volumetric determinations depends in part upon the accuracy attained in the measurements made, and this necessitates the use of certain special forms of apparatus, of which the most important are those described in the following paragraphs.

Burettes are calibrated glass tubes of uniform, small, diameter, designed to measure variable amounts of liquids delivered by them when supported in a vertical position. The delivery of the liquid measured, in the form first used by Geissler, is controlled by a glass stopcock, and in the form first used by Mohr, by a rubber joint, provided with a spring pinchcock or a screw clamp, which connects the end of the tube with a short glass nozzle. The former has the disadvantage of requiring the use of some lubricant, such as a mixture of beeswax and vaseline, and, even if so provided, will leak unless the key to the stopcock has been accurately ground. The latter has the disadvantage that the rubber connection is acted upon to some extent by certain reagents which may reduce the concentrations of the solutions of these reagents when measured in such a device. A more serious objection is that the flexible rubber wall is affected by varying pressure and therefore the capacity of the burette below the lowest graduation may be a trifle greater when full of liquid than when nearly empty. The burettes usually employed are designed to deliver either 100, 50, 25, or 10 cc. The 50-cc. burette should be graduated to read tenths of a cubic centimeter, and its diameter should be small enough to make each tenth correspond to at least 1 mm. in length.

becomes an exceedingly sharp point of reference from which to compare the graduations on the tube. If the liquid being measured is intensely colored the circle formed by the uppermost points on the curve of the meniscus forms the most satisfactory plane of reference with which to compare the graduations on the tube.

**Errors from Drainage.** When a liquid is permitted to pass out of a burette somewhat rapidly, small amounts adhere to its inner surface, and some of it gradually flows down and unites with the

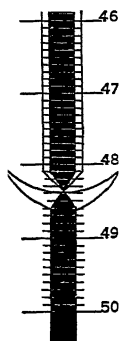


Fig. 53.—Schell-back burette.

liquid still remaining in the burette. The rapidity with which the level of the liquid in the burette attains its ultimate position depends upon the viscosity of the solution, the area and form of the surface drained, and the rapidity with which the solution has been permitted to flow from the tube. The viscosity depends in turn upon the chemical nature, concentration, and temperature of the solution. In order to avoid errors from this source, a sufficient interval must elapse between the time at which the flow from the apparatus is stopped and the time at which the reading is made. The minimum value of this time interval is easily ascertained by a series of simple experiments.

In the use of pipettes, both the drainage from the inner surface and the capillary action at the nozzle have to be considered, and a definite method of procedure must be adopted, for its calibration and use. The conditions which yield the most uniform results are obtained when the nozzle of the pipette is made to touch the side of the vessel into which the liquid is being delivered and to remain in contact with it for ten seconds after the main part of the liquid has been delivered. It is not advisable to blow out the few drops which are retained by the nozzle as the result of capillary action.

**Errors from Changes of Temperature.** A change in temperature affects both the size of the vessels used and the density of the liquid measured. The first effect is practically constant for temperatures ranging from 0° C. to 100° C. For glass vessels of the usual form this so-called "coefficient of cubical expansion" has the value 0.000025, which represents the increase in cubic

centimeters per cubic centimeter in the capacity of the vessel for an increase of 1° C.

The second effect is not constant, even over small ranges of temperature, and varies greatly with the liquid concerned. The expansion of the liquid is much greater than that of the containing vessel. All organic liquids show a large expansion as compared with water. The expansion of dilute aqueous solutions, such as are used in most volumetric determinations, does not differ greatly from that of pure water.

The actual error which results from the use of a piece of graduated apparatus at a temperature which differs from that at which it has been calibrated is due to the difference between the effect on the liquid and the effect on the containing vessel. It is a simple task to calculate, from the coefficient of cubical expansion of glass and from the density of water at different temperatures, a series of factors which represent the numbers by which the observed volume should be multiplied to correct for departures in temperature from that for which the apparatus was calibrated.

**Errors from Variation in Unit of Volume Employed.** If the same unit of volume is used in standardizing the solution as in making the actual determination, it makes no difference what that unit is. Several different units, most of which represent modifications of the standard metric unit, are in use. The standard liter,<sup>1</sup> the volume occupied by 1 kilogram of pure water at 4° C., is largely used. In order to calibrate a piece of apparatus in terms of this unit, when working under ordinary atmospheric conditions, it is necessary to correct the weight of water used for buoyancy and for the effect of temperature on both the water and the capacity of the vessel being calibrated. If  $1000x$  represents the weight in grams of brass needed to counterbalance the water whose volume at 20° C. is a standard liter, and if it is assumed that the density of water at 20° C. is 0.99823 gram, that of air is 0.0012 gram, and that of brass is 8.4 grams per cubic centimeter, the value of  $1000x$  can be calculated from the expression:

$$\left[ 1000x + \left( \frac{1000x}{0.99823} - \frac{1000x}{8.4} \right) 0.0012 \right] \div 998.23 = 1.$$

<sup>1</sup> This is the definition adopted by the Bureau of Standards [Circular No. 9, page 4 (1916)].

It can be calculated from this expression that  $1000x = 997.17$  grams.

Since the liter is too large for convenient use, a unit which is one one-thousandth as large is more generally employed. This unit should be called the milliliter (mil.), but through conventional usage extending over many years it is commonly designated the cubic centimeter (cc.). Actually it is greater by one part in 350,000 than the cubic centimeter, a difference which can be ignored except in very special kinds of measurements.

The so-called "Mohr unit" of volume is the space occupied by one kilogram of water when weighed in air with brass weights at a temperature of  $17.5^{\circ}\text{C}$ . Other units involving use of the same amount of water measured at  $15^{\circ}\text{C}$ . or  $20^{\circ}\text{C}$ . are in use. All of these units bear a simple numerical relation to the standard unit. The  $20^{\circ}\text{C}$ . unit is obviously  $(1 \div .99717)$  times the standard unit.

Much of the calibrated apparatus sold by manufacturers bears no mark by means of which the unit employed can be ascertained. Even if it is designated, errors of calibration are to be anticipated as the work is often done hastily, and also because in the calibration of burettes, it is customary to assume that the inner diameter of the tube is perfectly uniform. Further, there is no generally accepted method of procedure in the calibration of pipettes, and therefore a personal factor enters in their use. These facts make it desirable to calibrate every piece of measuring apparatus used unless it has been calibrated with a guaranteed degree of accuracy by someone working under carefully defined conditions. The Bureau of Standards at Washington calibrates certain forms of volumetric apparatus in terms of standard liters when measured at  $20^{\circ}\text{C}$ ., and the details of procedure used by it are fully described.

✓ **Factors for Temperature Corrections.** In this book the volume occupied by that amount of water which counterpoises 1 kilogram of brass, when measured at either  $15^{\circ}\text{C}$ . or, preferably, at  $20^{\circ}\text{C}$ . will be adopted and it is assumed that the apparatus used will be calibrated in terms of these units, depending upon the prevailing room temperature at the time the calibration is made. Since it is not always possible to make all subsequent measurements at the calibration temperature it is necessary to know, and possibly to correct for, the effect due to departures from that temperature.

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The correction can be expressed in the form of a factor, easily calculated from the coefficients of expansion of water and glass, by which the observed volume must be multiplied in order to give the volume which would have been observed if the calibration had been made at the proper temperature. These factors, for the temperature range between 10° C. and 25° C., are given in the following table:

Temperature of Actual Measurement	Factor for Apparatus Calibrated at 15° C.	Factor for Apparatus Calibrated at 20° C.
10° C.	1.00047	1.00124
11	1.00040	1.00117
12	1.00032	1.00109
13	1.00023	1.00100
14	1.00012	1.00089
15	1.0	1.00077
16	0.99987	1.00064
17	0.99972	1.00049
18	0.99956	1.00034
19	0.99940	1.00018
20	0.99923	1.0
21	0.99904	0.99981
22	0.99884	0.99961
23	0.99861	0.99941
24	0.99841	0.99919
25	0.99820	0.99897

The table shows that a variation of one degree in the temperature of measurement does not give rise to an error exceeding one part in 6000, and therefore the correction may in many cases be omitted.

**Accuracy of Volumetric Measurements.** No difficulty is experienced in making devices for the measurement of specific amounts of liquids to any desired percentage of accuracy by increasing the volume measured and decreasing the diameter of the tube in which the level of the liquid being measured is adjusted. In making devices for the measurement of indefinite volumes of liquids, this is not possible without using tubes whose length is so great as to make them unwieldy. With the usual type of

burette in which 1 cc. corresponds to 1 cm. of length, it is difficult to reduce the error of each observation to less than 0.04 cm. Assuming that the errors in both of the observations upon which the final measurement depends are not of the same sign, this would give rise to a total error of 0.08 cc., and even if 25 cc. of liquid are being measured the percentage error of this feature of the process becomes 0.32. It is difficult to reduce the errors of such measurements to values comparable with those of the weighings concerned in the same process. In order to make these errors as small as possible, the amount of sample used and the strength of the standard solution employed should be so related as to necessitate the use of an amount of standard solution nearly equal to the total capacity of the burette used. If a high degree of precision is demanded weight burettes, described on page 272, should be used.

### Procedure for Calibration of Volumetric Apparatus

**Cleaning Graduated Apparatus.** Unless the surface of the apparatus to be calibrated is perfectly clean, water and dilute solutions will not adhere to it as a film of uniform thickness, but will form streaks or drops, resulting in variations in the total amount retained by the walls after the liquid has been allowed to drain from them, and in the formation of a poorly defined meniscus. Films of greasy matter, which may come from the stopcock lubricant, or of dust derived from the air, or of precipitates derived from the solutions previously measured, are frequent causes of such difficulties. In order to reduce them to a minimum, all volumetric apparatus should be rinsed after use and kept protected from dust. The best reagents for removing films of an organic nature are caustic soda and "cleaning mixture." The latter is made by saturating sulfuric acid of 1.6 specific gravity with either chromic acid or sodium dichromate. The film of manganese dioxide, which sometimes appears in vessels in which permanganate solutions have been measured, is best removed by dilute hydrochloric acid, and that in which silver salts have been measured, by dilute ammonium hydroxide. As the cleaning mixture acts on rubber, and makes it hard and brittle, connections



which form a feature of the Mohr type of burette should be removed before this mixture is used. It will be found convenient to prepare a cylinder filled with the cleaning solution so that burettes and pipettes can be allowed to soak in it for any desired time.

**Setting Up and Reading the Burette.** The burette should always be supported in a perfectly vertical position by means of a suitable clamp and support. The glass tip should not be too long and should have a fine round opening. If closed by means of a pinchcock, the latter should be strong enough to prevent appreciable leakage during a five-minute interval even when full of liquid. Glass stopcocks which leak can be made tight by rotating the key, after it has been smeared with a small amount of fine carborundum powder, in the socket in which it is supposed to fit. Only the minimum amount of lubricant should be used on the stopcock. The graduation marks on burettes, which become obscure after long use, may be rendered more conspicuous by rubbing fine rouge, or any other deeply colored powder, into them.

Practice reading the level of water in a partially filled burette by one or more of the devices described on page 275. The effort should be made to read to within one-fiftieth of 1 cc. but this is often impossible. Determine the minimum length of time which must be allowed for drainage by filling with water to the zero point, allowing the water to flow rapidly from the delivery tube until its level reaches one of the lowest graduations, and noting the changes in level at intervals of one minute from the time of closing the pinchcock.

**Procedure for Calibrating Burettes.** Weigh accurately to 0.01 gram a dry 35-cc. weighing bottle or a small beaker with a watch-glass cover. Fill the burette with distilled water whose temperature does not differ by more than 1° from either 15° C. or 20° C. depending upon the normal temperature of the laboratory. Raise the delivery tube of the burette until nearly horizontal, and while in this position, open the pinchcock until the air bubble, which is sometimes present, has been driven out, then lower the delivery tube, and again open the pinchcock until the lowest point of the meniscus corresponds exactly with the zero point of the burette.

Place the delivery tube of the burette inside the weighing bottle, open the pinchcock, and allow 5 cc. of water to pass through it. Close the bottle and weigh as before, then read and record the exact position of the water in the burette. Continue to remove and weigh 5-cc. portions of the water until 25 cc. have been removed. Empty the water from the bottle, dry and again weigh, and then calibrate the remaining 25-cc. portion of the burette.

Prepare a table, of which one column represents the weights of water delivered between the zero point and the ten other points at which readings were made; a second column, the corresponding readings of the burette; and a third column, the figures in column one diminished by those in column two. The figures in the third column represent the corrections to be added to the apparent readings. If any of these errors amount to as much as 0.05 cc., calibrate the burette in the neighborhood of the point giving this error at intervals of 1 cc.

Finally prepare a graph showing the relation between the graduations on the burette and the corrections to be added. The scales on the two axes must be suitably chosen if the graph is to be usable.

**Procedure for Calibrating Pipettes.** Weigh to 0.01 gram a clean, dry weighing bottle of about 30 cc. capacity. Suck up pure water of the proper temperature into the 25-cc. pipette until the level of the liquid is above the mark on the stem. Close the upper end of the pipette with your finger, which should be perfectly dry, and then, by gently releasing the pressure, allow water to flow out until the lowest point on the curve of the meniscus corresponds to the mark on the pipette. Place the nozzle of the pipette in contact with the inner surface of the weighing bottle, and allow the water to flow into it. Drain for twenty seconds. Close the weighing bottle and weigh to 0.01 gram.

Calibrate the 10-cc. pipette in the same manner.

**Procedure for Calibrating Flasks.** Clean a 100-cc. and a 250-cc. flask and rinse with distilled water. Insert a long piece of glass tubing which is attached to a foot bellows, or other device for producing a blast of air, into the 250-cc. flask, hold the latter in an inclined position with the neck down, and slowly heat the body of the flask by means of a smoky flame, rotating the flask about

its axis until drops of moisture can no longer be recognized in the interior of the flask. Allow it to cool, clean the outside surface, and weigh accurately. Fill the flask with water at the standard temperature until the lowest point on the meniscus corresponds to the mark on the neck of the flask. Place on a balance designed to carry a load of at least 500 grams and weigh to 0.01 gram. Subtract the weight of the flask from the weight last obtained to find the capacity of the flask.

Calibrate the 100-cc. flask in a similar manner.

### Questions and Problems. Series 21

1. Calculate the factor which should be used in converting measurements made in a vessel calibrated to give 15° Mohr units into standard metric units, assuming that the density of water at 15° C. is 0.999099 gram, that of the brass weights used is 8.4 grams, and that of air is 0.0012 gram per cc. *Ans.* 0.9980.

2. Calculate the factor given in the table on page 279 for correction of measurements made at 20° C. in a vessel calibrated in terms of the 15° Mohr unit, assuming the coefficient of cubical expansion of glass is 0.000025 per degree and the density of water at 15° C. is 0.999099 gram and at 20° C. is 0.998203 gram per cc. *Ans.* 0.99922.

3. Exactly 18.23 cc. of 0.5 molal solution of hydrochloric acid are diluted with water to the mark on the neck of a flask supposed to represent 1 liter. It is subsequently found that this mark actually represents 999.74 cc. What is the normality of the solution? What percentage error would appear in all results obtained with the solution if no correction is made?

4. What is the error of a volumetric process in which the same percentage error is made in finding the volume of solution used for the titration as in weighing the sample, assuming that both errors have the same sign and that there is no error in the standardization?

5. A solution which has been standardized at a temperature of 15° C. by the use of a burette which was also calibrated for this temperature, was found to contain 0.02 gram of hydrochloric acid per cc. If some of this solution is measured out of the same burette at a temperature of 10° C. what weight of hydrochloric acid is present in each cubic centimeter as measured out?

6. In preparing a one-tenth normal solution of silver nitrate (which should contain 0.010788 gram of Ag per cc.) 5.7 grams of silver were weighed out, dissolved, and diluted to 500 cc. in a graduated flask. The solution in this flask was emptied into a bottle, which had not been dried and which contained 0.5 cc. of water adhering to its sides, and 0.4 cc. of the silver solution was left adhering to the flask. If 28.36 cc. of water was added to the bottle and the mixture shaken, what relation would the resulting mixture bear to one-tenth normal strength? *Ans.* 0.9991.

## 284 FUNDAMENTALS OF QUANTITATIVE ANALYSIS

7. The volume of water which remains adhering to a 500-cc. flask is 0.4 cc. How large a volume of a solution which is to be measured in it should be added to the flask for the purpose of rinsing it out so that the concentration of the original solution shall not be changed by more than one-hundredth of 1 per cent?

(*Note.*—This problem is most easily solved by letting  $x$  represent the volume of standard solution needed and setting up the equation which expresses the requirement named.)

8. In calibrating a burette by the procedure outlined on page 281, it is found that the correction is always positive and increases at a fairly uniform rate between the zero and the 50-cc. mark. How would you interpret these facts.

9. The inner diameter of the neck of a flask, on which a circular mark indicating the level of the liquid whose volume at  $15^{\circ}$  is one-fourth of a standard liter, has been inscribed, is 8 mm. It is desired to inscribe on it a second mark indicating the level of the liquid whose volume is one-fourth of a Mohr  $15^{\circ}$  unit. How many mm. of vertical distance should separate the two marks?

*Ans.* 11, 3.

## SECTION VII

### VOLUMETRIC PROCESSES INVOLVING PRECIPITATION

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#### CHAPTER XXIX

#### DETERMINATIONS WITH SOLUTIONS OF SILVER NITRATE

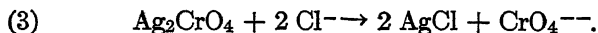
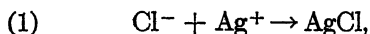
##### I. General Theory

**Silver Ion as a Precipitating Agent.** The salts of silver, with the exception of the nitrate and the sulfate, are distinguished by their slight solubility. The solubility products of the chloride, bromide, and iodide are  $1.1 \times 10^{-10}$ ,  $4 \times 10^{-13}$ , and  $1 \times 10^{-16}$  respectively. Even the largest of these is small enough to insure a practically complete reaction between the silver ion and any of the three halide ions, and a rapid rate of change in their concentration as the end point is approached when a solution of a soluble halide is titrated with a silver salt or vice versa. The curves representing this relation would indicate the probability of attaining a higher degree of accuracy than that of the ideal titration discussed on page 262. Although silver ion forms a number of complex ions, the tendency for the formation of complexes with the three halides is small, and adsorption of soluble halides by the silver compounds, though recognizable, is not large. This adsorption is greatest for the least negative iodide ion.

**Determination of End Points without an Indicator.** When silver chloride is made to separate from a solution as a precipitate it is very finely divided, and a minute quantity of it can be recognized owing to the opalescence which it imparts to the solution. If such a solution is shaken vigorously, the precipitate coagulates, leaving a liquid which is perfectly bright and clear. If, therefore,

a solution of a soluble chloride is titrated with a dilute solution of silver nitrate, and the mixture shaken in a well-stoppered bottle after every addition of the silver solution, the point at which the addition of a further quantity of silver fails to produce an appreciable opalescence can be recognized with a high degree of accuracy and, under certain conditions, can be used as the end point of the process. The method is tedious and demands skill and experience. A more convenient, but less accurate method, which depends upon the use of an indicator, is more frequently used. In making the reverse titration, that is, the determination of silver with a soluble halide, this method finds almost universal usage. It is possible to determine the fineness of silver bullion to within one part in two thousand by this procedure.

**Determination of End Points with a Chromate Indicator.** The insoluble chromate of silver has an intense red color and small amounts of it are easily recognized even when associated with any of the three halides of silver, or with a solution of a soluble chromate. The molal solubility of silver chromate is about five times that of silver chloride, and very much greater than that of the bromide or iodide. This suggests the possibility of using the chromate ion to ascertain when the concentration of any of the three halide ions has been reduced to a small value in making titrations of solutions containing these ions. Such a procedure would involve three equilibria and three rates of reaction, namely:



The equilibrium constant for (3) depends upon the relative values of the constants for (1) and (2) but there is no necessary relation between the rates at which the three processes take place. Experience shows that in making such a titration it is not possible to immediately effect a uniform admixture of the two reagents and hence silver chromate separates even though ( $\text{Cl}^-$ ) has not been reduced to the value demanded if a true equilibrium was attained. This precipitate must disappear owing to reaction (3) if a correct

result is to be obtained and therefore the rate of reaction (3) is an important factor in the process.

The changes which take place can be easily followed quantitatively by some simple calculations. When silver ion is added to a solution containing both chloride and chromate ion, a very slight amount of silver produces a precipitate of silver chloride. As further quantities of silver are added and silver chloride continues to separate, the value of  $(\text{Cl}^-)$  must decrease, and, since  $(\text{Ag}^+) \times (\text{Cl}^-)$  must always equal the solubility product of silver chloride, namely  $1.1 \times 10^{-10}$ , the value of  $(\text{Ag}^+)$  must increase. A point is finally reached at which  $(\text{Ag}^+)^2 \times (\text{CrO}_4^{--})$  equals  $1.7 \times 10^{-12}$ , that is, the solubility product of silver chromate, and the mixture must then begin to acquire a red color. At the true end point both  $(\text{Ag}^+)$  and  $(\text{Cl}^-)$  must equal  $1.05 \times 10^{-5}$ , and, if the apparent end point is to coincide with the true end point, silver chromate should begin to separate when  $(\text{Ag}^+)$  has attained the value  $1.05 \times 10^{-5}$ . This requirement can be satisfied by making  $(\text{CrO}_4^{--})$  have a particular value, namely the value found by dividing the solubility product of silver chromate by the square of the silver ion concentration at the true end point, that is,  $1.7 \times 10^{-12} \div (1.05 \times 10^{-5})^2$  or  $1.5 \times 10^{-2}$ . The amount of soluble chromate which must be present in order to give  $(\text{CrO}_4^{--})$  this value is large. If potassium chromate is used, and if it is assumed that all of the salt is dissociated, each 100 cc. of solution would have to contain 0.291 gram. This concentration is sufficient to impart a deep yellow color to the solution. Reducing  $(\text{CrO}_4^{--})$ , however, produces a much smaller change in the point at which silver chromate separates than might be anticipated since it depends upon the second power of  $(\text{Ag}^+)$ . If, for example,  $(\text{CrO}_4^{--})$  is given the value  $1.5 \times 10^{-3}$ ,  $(\text{Cl}^-)$  becomes  $0.32 \times 10^{-5}$ , that is, reducing  $(\text{CrO}_4^{--})$  to one-tenth reduces  $(\text{Cl}^-)$  to about one-third. Furthermore, the total volume of standard solution needed to change  $(\text{Cl}^-)$  from  $1.05 \times 10^{-5}$  to  $0.32 \times 10^{-5}$  is small; it can be calculated to be less than one drop of a tenth normal solution if the total volume of the mixture is 100 cc.

If the titration is continued after the true end point is reached, both silver chromate and silver chloride continue to separate, but, since the solution is saturated with both the chloride and the

chromate, the ratio of  $\text{Cl}^-$  to  $\text{CrO}_4^{--}$  is fixed. It can be calculated as follows:

$$(\text{Ag}^+) (\text{Cl}^-) = (1.05 \times 10^{-5})^2 \text{ or } (\text{Ag}^+)^2 = \frac{(1.05 \times 10^{-5})^4}{(\text{Cl}^-)^2}$$

$$(\text{Ag}^+)^2 (\text{CrO}_4^{--}) = 1.7 \times 10^{-12} \text{ or } (\text{Ag}^+)^2 = \frac{1.7 \times 10^{-12}}{(\text{CrO}_4^{--})}$$

Since both equations relate to the same solution  $(\text{Ag}^+)^2$  has the same value for both equations and hence

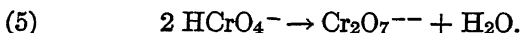
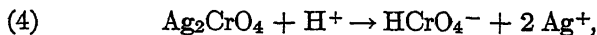
$$(1.05 \times 10^{-5})^4 \div (\text{Cl}^-)^2 = (1.7 \times 10^{-12}) \div (\text{CrO}_4^{--})$$

or

$$(\text{CrO}_4^{--}) : (\text{Cl}^-)^2 :: 1.52 \times 10^8 : 1.$$

It should be noted also that a certain minimum amount of silver chromate must be formed before it can be recognized with certainty. This minimum depends upon the total volume of the mixture, the amount of silver chloride and the extent to which it is coagulated, and the ability of the analyst to recognize slight color changes. This discussion indicates that although a relatively large amount of indicator should be used in the titration, moderately large variations in this amount produce a comparatively slight effect upon the final result. It is also evident that a personal factor is involved in the titration, and it is desirable to eliminate this as far as possible by standardizing the silver solution with a known weight of a pure chloride, and making all determinations under exactly the same conditions as were adopted in the standardization.

**Effects of Acids upon the Titration.** Although moderate concentrations of even largely dissociated acids do not affect reaction (1) appreciably, very slight concentrations affect reaction (2) to such an extent as to make it impossible to determine the true end point with even approximate accuracy. This can be explained by considering the reactions which take place when silver chromate is treated with a strong acid, namely:

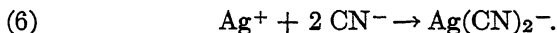




Both of these reactions have been studied quantitatively.<sup>1</sup> The equilibrium constant for (4) depends upon the constant which determines the hydration of chromate to hydrochromate ion, that is  $(\text{HCrO}_4^-) \div (\text{H}^+) (\text{CrO}_4^{--})$ , which has the value  $1.2 \times 10^6$ . The constant for (5), that is  $(\text{Cr}_2\text{O}_7^{--}) \div (\text{HCrO}_4^-)^2$ , has the value 74. The combined effect of these reactions is to decrease  $(\text{CrO}_4^{--})$  by an amount which nearly equals the total amount of  $\text{H}^+$  added. As the solubility product of silver dichromate has the value  $2 \times 10^{-7}$ , it is not probable that this salt will separate. Still another effect results from the fact that  $\text{Cr}_2\text{O}_7^{--}$  imparts a red instead of a yellow color to the solution, and materially increases the difficulty of recognizing small amounts of silver chromate.

The presence of small amounts of hydroxyl ion is not objectionable provided the concentration is not great enough to cause the solubility product of silver hydroxide to be exceeded. If the solution is made neutral to an indicator such as litmus or rosolic acid no difficulty from either  $\text{H}^+$  or  $\text{OH}^-$  will be experienced.

**Reaction between Silver Ion and Cyanide Ion.** A solution of silver nitrate is also used for the determination of soluble cyanides. When silver ion is added to a solution containing cyanide ion, a complex ion is formed as represented by the equation:



The equilibrium constant for this reaction, that is

$$(\text{Ag}(\text{CN})_2^-) \div (\text{Ag}^+) \times (\text{CN}^-)^2,$$

is  $1 \times 10^{21}$ , and therefore the amount of silver left in the form of a simple ion must be extraordinarily small when equivalent amounts of the two reagents are used. If it is assumed that 50 cc. of a 0.1 molal solution of soluble cyanide is titrated with a 0.1 molal solution of silver nitrate, the true end point is reached when 25 cc. of the nitrate solution have been used. If, further, it is assumed that the total volume of the mixture at the true end point is 100 cc., the total molal concentration of cyanide and silver salt is 0.05 and 0.025 respectively. If the fraction of cyanide ion

<sup>1</sup> Sherrill, Jour. Am. Chem. Soc., 29, 1673 (1907).

and silver ion which combine is represented by  $x$ , the complex ion formed must be represented by  $.025x$ , the silver ion left by  $(1 - x).025$ , and the cyanide left by  $(1 - x).05$ . By substituting these values in the equilibrium expression we get

$$0.025x = (1 - x).025 \times (1 - x).05 \times (1 - x).05 \times (1 \times 10^{21}),$$

and therefore

$$[(1 - x).025]^3 = .025x \div 4 \times (1 \times 10^{-21}),$$

and

$$(1 - x).025 \quad \text{or} \quad (\text{Ag}^+) = 1.84 \times 10^{-8}.$$

As the silver ion is added there is at first no visible evidence of the progress of the reaction, but, as the concentration of the cyanide ion is reduced, the separation of the compound  $\text{Ag}_2(\text{CN})_2$  becomes possible. Since the solubility product of this compound, namely  $(\text{Ag}^+) \times (\text{Ag}(\text{CN})_2^-)$ , is  $2.25 \times 10^{-12}$ , and the concentration of  $\text{Ag}(\text{CN})_2^-$  approaches the value 0.025, the value of  $(\text{Ag}^+)$  at which it should separate is approximately

$$2.25 \times 10^{-12} \div 0.025 = 1 \times 10^{-10}.$$

This means that  $\text{Ag}_2(\text{CN})_2$  should begin to separate slightly before the true end point is reached. The actual difference between the two concentrations is so small, and the rate of change in  $(\text{Ag}^+)$  is so great as the true end point is approached that the difference can be safely disregarded. The appearance of this compound as a permanent precipitate might therefore be used to ascertain the end point of the process, and it is so used. Unfortunately the precipitate has the property of coagulating almost immediately and is only very slowly acted upon by a moderate excess of cyanide ion. Since small amounts of precipitate are necessarily found before the true end point is reached, owing to imperfect admixture of the two reagents, the determination of the end point is both tedious and inaccurate. Much better results can be obtained by the addition of a small amount of iodide ion as an indicator.

Silver iodide is less soluble and more difficult to coagulate than  $\text{Ag}_2(\text{CN})_2$ , and when freshly precipitated an extremely small

amount of it can be easily recognized. Since its solubility product is  $1 \times 10^{-16}$  it should separate, along with  $\text{Ag}_2(\text{CN})_2$ , in the mixture described above if the value of  $(\text{I}^-)$  is as great as  $1 \times 10^{-16} \div 1 \times 10^{-9} = 1 \times 10^{-7}$ , and a larger concentration should insure separation of  $\text{AgI}$  rather than  $\text{Ag}_2(\text{CN})_2$ . Actual experience with this procedure for recognition of the end point has shown that some  $\text{Ag}_2(\text{CN})_2$  may separate temporarily even if the excess of iodide is large. This difficulty is eliminated however by introducing ammonium hydroxide. Since this reagent also forms a complex with silver ion its presence must affect all the equilibria concerned, and should be expected to delay the appearance of both  $\text{AgI}$  and  $\text{Ag}_2(\text{CN})_2$ . Experiments<sup>1</sup> with known amounts of cyanides have shown that correct results are obtained if the mixture titrated contains about 8 cc. of 6 N ammonium hydroxide and 2 cc. of a 5 per cent solution of potassium iodide, if the final volume of the mixture does not exceed 100 cc. Under these conditions the end point is very well defined.

## II. Preparation and Standardization of a Solution of Silver Nitrate

**Concentration of the Solution.** The equivalency of silver ion, when used for the precipitation of the three halides of silver, is obviously one. Owing to the delicacy of the method used for the recognition of the end points in these titrations, a one-tenth normal solution is strong enough to insure a high percentage of accuracy. The reaction used for the determination of cyanides involves metathesis, although no precipitate is formed. There is no objection to assuming that the equivalency of silver ion is one in this reaction also, but, if this assumption is made, the equivalency of the cyanide ion is one-half, and the weight in grams of sodium cyanide equivalent to a liter of normal silver solution becomes twice the molecular weight of sodium cyanide. The extreme delicacy of the end point with the iodide indicator justifies the use of a tenth normal solution of silver nitrate for this determination also.

<sup>1</sup> Sharwood, Jour. Am. Chem. Soc., 19, 400 (1897).

**Choice of Method.** Silver nitrate of a high degree of purity is easily obtainable and, as it is not hygroscopic, can be weighed out accurately. Some samples yield solutions which are distinctly acid and these should be heated to the fusion point before being used. The salt fuses at  $198^{\circ}\text{C.}$ , at which temperature it begins to decompose, forming silver oxide. Care should be taken therefore to heat it to the point at which it barely fuses and allow to cool without delay.

Pure silver which is 999 fine is also easily obtainable and is frequently preferred to the nitrate for the preparation of standard silver solutions, as it dissolves rapidly in dilute nitric acid, and the excess of acid used can be eliminated by evaporating to dryness and cautiously heating the residual salt.

**Procedure for the Preparation of Tenth Normal Silver Nitrate Solution.** Weigh out accurately from 5.4 to 5.8 grams of pure metallic silver, place in a casserole or porcelain dish, cover with a watch glass, and add 20 cc. of dilute nitric acid. If action does not begin to take place after a few minutes, or if it is too slow, warm gently or add a small amount of concentrated nitric acid. When the metal is dissolved rinse off the under side of the watch glass, then place on the steam or sand bath, and evaporate the solution to complete dryness. If the sand bath is used, the mixture must be stirred during the later stages of the evaporation to avoid losses from spattering. Finally raise the temperature to the point at which the nitrate just fuses, noting that since the solubility curve terminates in the fusion curve, and the molten nitrate forms a nearly colorless liquid, this transition may escape recognition. The complete absence of white fumes when air is blown over the hot dish is sufficient evidence of the complete removal of nitric acid.

Allow the dish to cool, dissolve the salt in a little water, and transfer the solution to a 500-cc. graduated flask, using the rinsings of the dish to dilute to exactly 500 cc. Place a cork in the flask and invert several times, or until the mixture is homogeneous, then transfer to a clean glass-stoppered bottle which has been allowed to drain for about five minutes. Calculate the volume to which the silver weighed out should be diluted to make the residual solution exactly one-tenth normal, that is, to make 1 cc. contain 0.010788 gram of silver. Add to the bottle from a burette the

necessary amount of water, and then shake thoroughly. Test the solution with a piece of blue litmus paper for acidity. If it gives a perceptible reaction the solution must be neutralized by adding cautiously very dilute sodium hydroxide. The small amount of insoluble precipitate formed should be filtered off.

**Procedure for the Standardization.** Weigh out from 0.23 to 0.28 gram of pure, recently dried sodium chloride into a 200-cc. Erlenmeyer flask, add 35 cc. of water and 1 cc. of a 5 per cent solution of pure potassium chromate. Rinse out a clean 50-cc. burette with 10 cc. of the silver solution, discarding the rinsings, and then fill to the zero mark.

Add the silver nitrate solution to the salt solution somewhat rapidly until the red precipitate which forms temporarily disappears slowly, then add the silver solution more slowly until the mixture acquires a faint but permanent reddish tinge. If shaken vigorously, the red chromate of silver may separate with the silver chloride instead of remaining suspended. Its presence may be recognized with a greater degree of certainty if the titration is made in artificial light and a white background is used.

Calculate the weight of sodium chloride found to be equivalent to 1 cc. of the silver solution and divide by the weight of sodium chloride in 1 cc. of a normal solution of sodium chloride to obtain the normality factor.

### III. Determination of Chlorides in Soluble Salts

**Preliminary Statements.** The determination of chlorides in mixtures of soluble salts is one of the problems frequently presented to the analytical chemist and is usually solved by dissolving a known weight of the mixture and determining the chloride ion either gravimetrically, as described on page 178, or volumetrically. If titrated with a silver solution, using a chromate indicator, the solution must be carefully neutralized. The method is not affected by the presence of moderate concentrations of nitrates or sulfates, but is inaccurate in the presence of bromides, iodides, cyanides, and many of the salts of organic acids.

**Procedure.** Weigh out a sufficient amount of the sample to require the use of at least 20 cc. of the standard silver solution.

This may necessitate making a preliminary approximate estimation using at least 0.2 gram. Dissolve in 50 cc. of water and test for neutrality by bringing a stirring rod moistened with some of the solution into contact with pieces of red and blue litmus paper. If acid add very dilute sodium hydroxide, if basic very dilute nitric acid, until neutral. Next add 1 cc. of the chromate indicator and titrate with the silver solution exactly as in the standardization. Calculate the percentage of chloride present.

#### IV. Determination of Chloride Ion in Tap Water

**Preliminary Statements.** The concentration of the chloride ion in well or river water varies greatly, and its determination often yields results of much significance in deciding whether a sample is suitable for domestic use, for irrigation, or for the production of steam. Usually the amount present is relatively small and it is necessary to measure out from 200 to 500 cc. for the determination. The volume of silver solution required to produce a recognizable amount of silver chromate is much larger than in the preceding titrations, even if the concentration of the indicator is made the same. It is necessary therefore to make a correction for the amount of silver needed to saturate the solution with silver chromate. The value of the correction can be found by ascertaining the volume of standard silver solution needed to give the same color as that of the sample titrated when added to an equal volume of distilled water and chromate indicator. In order that the conditions of the two titrations may be as nearly identical as possible a small amount of some white precipitate, such as zinc oxide or calcium carbonate, is added to the distilled water to produce an effect similar to that of the precipitated silver chloride in the sample. Even if this correction is made, the volume of silver solution used is so small that the percentage error of the process is large. It can be reduced by using a more dilute solution of silver nitrate or by concentrating the sample before making the titration.

**Procedure.** Test the sample for alkalinity with litmus paper. Measure out 250 cc. into a 400-cc. Erlenmeyer flask, and, if necessary, neutralize with dilute nitric acid. Next add 5 cc. of the chromate indicator and titrate with the silver solution until a recognizable amount of silver chromate is produced. Set the

flask aside to use as a color comparison standard. Measure out 250 cc. of distilled water, add about 0.2 gram of zinc oxide or calcium carbonate and 5 cc. of chromate indicator, and titrate with the silver solution until it shows a color exactly similar to that of the color standard. Subtract the volume used in titrating the water from that used in titrating the sample, and calculate the weight of chloride ion present in 1 liter of water.

### V. Determination of Potassium Cyanide in Commercial Cyanide

**Preliminary Statements.** The commercial "cyanide" which is largely used for the extraction of gold and silver from their ores consists of a mixture of sodium and potassium cyanides together with small amounts of carbonates, chlorides, ammonium salts, and hygroscopic water. As sodium and potassium cyanide are about equally efficient solvents for the treatment of gold and silver ores, it is customary in the evaluation of such cyanides to determine the total cyanogen and to calculate the corresponding amount of potassium cyanide. As the cyanide is extremely hygroscopic, it is somewhat difficult to secure an average representative portion of a large sample, unless a large amount is taken for the analysis, dissolved in water, and a fractional part of the solution used for the analysis. Great care should be exercised in handling the sample, as it is extremely poisonous.

**Procedure.** Crush several pounds of the original sample until the particles do not exceed grains of wheat in size, place at once in a glass-stoppered bottle, and rotate and shake the latter until thoroughly mixed. Add about 5 grams of the sample to a weighing bottle and weigh accurately. Transfer the salt to a 250-cc. graduated flask, dissolve in water, dilute to exactly 250 cc., and mix thoroughly. Remove a 25-cc. pipette full of the solution to a 200-cc. Erlenmeyer flask, being very careful to avoid getting any of the solution into the mouth; add 8 cc. of dilute ammonium hydroxide, then 2 cc. of a 5 per cent solution of potassium iodide, and finally titrate with the silver solution until a very faint but permanent turbidity, due to the formation of silver iodide, appears. The accuracy of the determination can be increased by holding the flask against a black background while determining the end

point. Calculate the percentage of potassium cyanide present from the volume of silver solution required, noting that  $E$  of the general formula has the value one-half.

## VI. Questions and Problems. Series 22

1. What volume of a one-tenth normal solution of silver nitrate would be required to saturate 100 cc. of a solution which contained 0.3 gram of potassium chromate with silver chromate, assuming that the solubility product of silver chromate is  $1.70 \times 10^{-12}$ ? *Ans.* 0.01 cc.

2. If a standard solution of silver nitrate was used to titrate a solution containing bromide ion, what concentration of potassium chromate should be present in order to cause silver chromate to separate as soon as an equivalent amount of silver nitrate had been added, assuming that the solubility product of silver bromide is  $0.49 \times 10^{-14}$ ? *Ans.* 350.

3. The concentration of chloride ion in a solution which is saturated with AgCl, and which has a volume of 100 cc., is  $1 \times 10^{-6}$ . What volume of 0.1 normal silver nitrate solution would it be necessary to add in order to reduce the concentration to  $1 \times 10^{-8}$ ? Note that some of the silver added must be precipitated. *Ans.* 0.11 cc.

4. The solubility product of silver oxalate is  $1 \times 10^{-12}$ . If a solution of a soluble oxalate were titrated with a solution of silver nitrate what would be the concentration of silver ion at the true end point? *Ans.*  $1.28 \times 10^{-4}$ .

5. A solution of silver nitrate, which has been standardized by titrating against a sample of sodium chloride supposed to be pure, is found to be exactly 0.1 normal. It is subsequently found that the sample contains 1 per cent of potassium chloride. What is the actual normality of the solution? *Ans.* 0.0998.

6. A solution of silver nitrate contains exactly 0.015 gram of  $\text{AgNO}_3$  per cc., and 24 cc. of it are required to precipitate the chlorine in 0.5 gram of a sample which contains  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Calculate by the general formula the percentage of this salt present. *Ans.* 51.76.

7. It is found that 30 cc. of the silver nitrate solution referred to above are needed to react with the cyanide in 0.7 gram of a sample which contains  $\text{Ca}(\text{CN})_2$ . Calculate in like manner the percentage of this salt present. *Ans.* 34.82.

8. The volume of tenth normal silver nitrate solution used in titrating 0.5 gram of a sample of kainite is 35 cc. If one drop (0.04 cc.) of this volume is used in producing a recognizable amount of  $\text{Ag}_2\text{CrO}_4$ , what percentage error and what departure from the correct result for Cl does it cause? *Ans.* 0.11 and .03.

9. A liter of brine solution was added to a tank containing an unknown volume of water and the mixture stirred. If the original brine contained 100 grams of sodium chloride per liter, and the resulting solution 0.2 gram per liter, what was the volume of water? *Ans.* 499 liters.



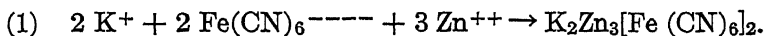
## CHAPTER XXX

### DETERMINATION OF ZINC WITH SOLUTIONS OF POTASSIUM FERROCYANIDE

#### I. Theory upon Which the Method Depends

**The Reaction Concerned.** When a dilute solution of potassium ferrocyanide is slowly added to a solution of a zinc salt a flocculent precipitate of a bluish color separates, but a point is finally reached at which the precipitate becomes pulverulent and pure white. The precipitate finally obtained contains both potassium and zinc, the relative amounts of which may vary according to the conditions under which the precipitate separates. It is not known whether a double ferrocyanide of zinc and potassium is formed or whether potassium ferrocyanide is adsorbed by the zinc ferrocyanide which first separates.

In devising a method for the determination of zinc based upon this reaction it is necessary to adopt certain standard conditions, and a preliminary study of the manner in which varying conditions affect the reaction is a necessary prerequisite to the intelligent use of the reaction. Under the conditions which are here adopted the reaction is represented with approximate accuracy by

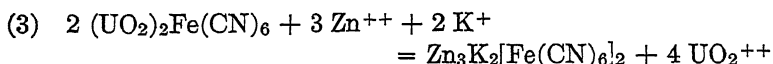


**Determination of the End Point.** When a soluble ferrocyanide is added to an iron salt a deep blue, or when added to a salt of copper, cobalt or uranyl a deep red-brown, precipitate separates. It is possible to recognize a smaller amount of a soluble ferrocyanide by means of a uranyl salt than of the other salts mentioned and these salts form the best indicators for this titra-

tion. The reaction with a uranyl salt is probably represented by



If a solution of potassium ferrocyanide is added to one which contains approximately equivalent concentrations of salts of both zinc and uranyl, both reactions (1) and (2) can be shown to take place, and further, if a solution containing zinc and potassium chlorides is added to a solution which contains suspended uranyl ferrocyanide, the latter is not affected. This indicates that the factor which determines the completeness of the reaction



has a comparatively small value or that the velocity is small. On the other hand, reaction (3) does not proceed in the reverse direction, at least when the time allowed is short, and a solution of a uranyl salt can be used to test a solution which is being titrated, for potassium ferrocyanide, since the addition of a uranyl salt will not produce a precipitate of uranyl ferrocyanide unless an excess of potassium ferrocyanide is present. In using a uranyl salt as an indicator, however, it is necessary to remove portions of the solution from time to time during the progress of the titration and bring it into contact with a drop of the indicator solution.

Since it may be necessary to make a large number of these tests before the true end point is reached, and since that portion which is removed cannot be returned to the main solution without producing a permanent precipitate of uranyl ferrocyanide, the total amount of zinc taken out may represent a rather large error. This error is small if the analyst has an approximate idea of the total amount of zinc present and can safely add sufficient ferrocyanide to precipitate most of the zinc before beginning to test the solution. When the amount present is entirely unknown it becomes necessary to divide the solution into a number of fractional parts and use one of these for an approximate determination, that is, to titrate by the addition of 1 or 2 cc. of the standard solution at a time; a second portion is then titrated to within 1 or 2 cc. of the required amount at once and completed by the addition of 0.1 cc. at a time. This method of determining an end

point which involves the use of an "outside" indicator is necessarily tedious, but is the best method known for this titration.

It is found that from 0.5 to 0.7 of the ferrocyanide solution usually employed must be added to 200 cc. of water before a clearly recognizable test is produced with the indicator. If all titrations are made with the same volume of solution the error from this source is constant, and if all the solutions titrated contain the same amount of zinc the error bears the same relation to the total amount of zinc represented. Suppose, for example, the ferrocyanide solution is standardized, by titrating a solution which contains 0.150 gram of zinc and has a volume of 200 cc., and that 30 cc. are required to react with the zinc. The total volume of solution required would be 30.5 cc. and the apparent value of each cubic centimeter  $150 \div 30.5$ , or 0.004918. If now this solution is used to titrate a zinc solution which has a volume of 200 cc. and contains 0.05 gram a volume of 10.5 cc. would be required and the calculated amount of zinc would be  $10.5 \times 0.004918$ , or 0.0516 gram. That is, an error of 1.6 mg. results, which would have been avoided if 0.5 cc. had been subtracted from the volumes of ferrocyanide solution used in the two titrations.

**Effect of Varying Temperature upon the Process.** In the experiments, the results of which are recorded below, a zinc solution containing 0.005 gram of zinc per cubic centimeter was titrated with a ferrocyanide solution containing 21.6 grams of  $K_4Fe(CN)_6 \cdot 3H_2O$  per liter at varying temperatures.

ZnCl <sub>2</sub> sol.	(NH <sub>4</sub> )Cl	HCl (conc.)	H <sub>2</sub> O	Temp.	Volume of K <sub>4</sub> Fe(CN) <sub>6</sub> sol.
cc.	grams	cc.	cc.	Degrees	cc.
30	5	5	140	20	25.5
30	5	5	140	50-45	29.85
30	5	5	140	80-75	29.85
30	5	5	140	100-95	30.02

The results show that, although the ratio between the volume of zinc solution used and the volume of ferrocyanide solution

needed to react with it decreases when the temperature is increased from 20° C. to 100° C., it is constant between 45° C. and 85° C. In the practical use of this method it is very desirable to adopt, among other standard conditions, a temperature at which the ratio is as nearly constant as possible, since it is not always convenient to maintain a particular temperature throughout an entire titration. It should also be noted that at 20° C. it is much more difficult to recognize the true end point than at any of the higher temperatures. A temperature of 80° C. can be advantageously adopted for one of the standard conditions.

**Effect of Varying Concentrations on the Process.** The effect of varying the concentration of the zinc salt, while maintaining the same concentration of hydrochloric acid and ammonium chloride, is shown in the results of the experiments recorded in the following table.

ZnCl <sub>2</sub>	(NH <sub>4</sub> )Cl	HCl (conc.)	H <sub>2</sub> O	Temp.	K <sub>4</sub> Fe(CN) <sub>6</sub> Used
cc.	grams	cc.	cc.	Degrees, C.	cc.
30	1.25	1.25	12.5	80	29.5
30	2.50	2.50	55.0	80	29.70
30	3.75	3.75	97.5	80	29.75
30	5.0	5.0	140.0	80	29.80
30	7.50	7.50	225.0	80	30.01

The slight increase in the volume of ferrocyanide solution used with increasing dilution is undoubtedly due to the larger amount of ferrocyanide required to produce a sufficient concentration of the latter to yield a recognizable test with the uranyl indicator. There is no reason to believe that the ratio here concerned varies, provided the concentration of the other reagents remains constant. Convenience alone should therefore determine the best volume to use for the titration. Since in the actual application of the method the zinc must usually be separated from other metals and a large volume of solution is necessarily obtained a volume of 200 cc. is a desirable standard to adopt.

**Effect of the Hydrogen Ion on the Process.** In titrating a solution of a zinc salt with a solution of a ferrocyanide the end

point is much more accurately determined when the solution contains a small amount of acid than when perfectly neutral. The presence of sufficient acid also assists in bringing about the change from a blue flocculent to a white pulverulent precipitate, which is a desirable feature. Further, when lead is present in the zinc solution the presence of sufficient acid suppresses the formation of insoluble lead ferrocyanide, and makes it possible to titrate zinc in the presence of this element.

The effect of varying concentrations of hydrochloric acid on the titration is shown in the following table.

ZnCl <sub>2</sub> Sol.	(NH <sub>4</sub> )Cl	HCl (conc.)	H <sub>2</sub> O	Temp.	K <sub>4</sub> Fe(CN) <sub>6</sub> Used
cc.	grams	cc.	cc.	Deg., C.	cc.
30	5	0	145	80	±29.4
30	5	1	144	80	±29.8
30	5	5	140	80	29.90
30	5	10	135	80	30.10
30	5	25	120	80	31.50
30	5	50	95	80	32.50

These results show a gradual increase in the volume of ferrocyanide solution required for the same amount of zinc with increasing concentration of acid although the rate of increase is not large. Both very large and very small amounts of acid greatly increase the difficulty of obtaining accurate end points and indicate the desirability of adopting for one of the standard conditions 5 cc. of the acid for each 200 cc. of solution.

**Preparation and Standardization of the Solution.** This method is very widely used for the determination of zinc in ores and alloys, and it is found desirable to make 1 cc. of the ferrocyanide solution used equivalent to 0.005 gram of zinc, that is, to prepare it according to the unitary rather than according to the normal system. Under the conditions already adopted as standard, that is, where the temperature at the beginning of the titration is 80° C., the volume before titration is 200 cc., and where 5 grams of ammonium chloride and 5 cc. of concentrated hydrochloric acid are present it is found that a solution of potas-

sium ferrocyanide containing 21.6 grams of the crystallized salt per liter will precipitate 0.005 gram of zinc per cubic centimeter. The exact value of the solution should be determined by titrating against a known amount of zinc. Either pure metallic zinc or pure zinc oxide, which has been recently ignited to convert any zinc carbonate which it may contain into zinc oxide, are used for the standardization.

The ferrocyanide solution is not a very stable one and may show an appreciable change in standard even after standing for a week, which necessitates frequent restandardization. An appreciable tendency for the ferrocyanide to change into ferricyanide, which results in less clearly defined end points, is also recognizable.

## II. Application of the Method to the Analysis of Zinc Ores

**Preliminary Statements.** Most of the important ores of zinc contain that element as sphalerite ( $\text{ZnS}$ ) or smithsonite ( $\text{ZnCO}_3$ ), both of which are easily dissolved by concentrated hydrochloric acid; in certain classes of ores it is present as calamine ( $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ ), which is but slowly or imperfectly decomposed by treatment with acids and such ores must usually be fused with some basic substance such as sodium carbonate to render them easily soluble.

All classes of zinc ores invariably contain silica or insoluble silicates, iron in the form of pyrites, and very often lead, copper, cadmium and manganese, also, as sulfides. As the zinc in such mixtures is frequently intimately associated with the other sulfides it is usually necessary to decompose these minerals also, in order to insure complete solution of the zinc, which necessitates treatment with nitric as well as hydrochloric acid.

**Separation of Zinc in Simple Ores.** When the ore does not contain copper or cadmium, and where the percentage of iron is small as compared with the zinc, the latter can be separated with a sufficient degree of accuracy for the ferrocyanide titration by the use of ammonium hydroxide and bromine. The separation of zinc from iron by the use of ammonium hydroxide is unsatisfactory, owing to the occlusion of zinc by the ferric hydroxide precipitate, but where the total amount of iron does not exceed 0.1 gram a double precipitation usually suffices to give a satis-

factory separation. Manganese if present in small amounts is usually completely precipitated with the iron as the dioxide, if a moderate excess of bromine water is also added. The excess of bromine thus added to the zinc-containing filtrate must, however, be driven off by evaporation before titration with the ferrocyanide solution, as it readily oxidizes ferrocyanide to ferricyanide.

### III. Outline of Method for the Preparation and Standardization of the Ferrocyanide Solution

**Preparation.** Weigh out 21.63 grams of crystallized potassium ferrocyanide, dissolve in water and dilute to 1000 cc.

**Titration of a Known Weight of Zinc.** Ignite about 2 grams of pure zinc oxide in a platinum or porcelain crucible for twenty minutes at a red heat and then allow to cool. Weigh out 0.25 gram of the ignited oxide into a 400-cc. beaker, add 10 cc. of dilute hydrochloric acid and warm until dissolved. Neutralize the solution with ammonium hydroxide, add 5 cc. of concentrated hydrochloric acid and then dilute to 200 cc. Heat the solution thus obtained to 80° C. and add somewhat slowly 38 cc. of the ferrocyanide solution. Complete the titration by adding the ferrocyanide solution in quantities of not more than four drops at a time, and after vigorous stirring bringing a drop of the mixture into contact with a drop of a 5 per cent solution of uranyl acetate, which has been previously placed on a white porcelain plate or a sheet of glazed white paper. The drop of solution taken for the test should be mixed thoroughly with the drop of indicator, but the rod should be wiped or rinsed off before it is again placed in the solution which is being titrated. The true end point represents the point at which a slight but clearly defined brownish tinge can be recognized with certainty. The intensity of the color finally adopted as the true end point should be carefully noted, and all subsequent titrations should be carried to the same color shade. As the intensity of this color increases on standing, an effort should be made to allow the same time interval to elapse between the first admixture of the 2 drops and the final decision as to whether the end point has been reached.

**Determination of Excess Required for the End Point.** To a second beaker add 10 cc. of dilute hydrochloric acid, sufficient ammonium hydroxide to neutralize it and then 5 cc. of concentrated hydrochloric acid. Dilute the mixture to 240 cc., heat to 80° C. and titrate with the ferrocyanide solution as before, noting that the absence of the white potassium-zinc ferrocyanide precipitate may decrease slightly the excess of ferrocyanide required to produce a color shade as intense as that adopted in the previous titration.

**Calculation of Value of Ferrocyanide Solution.** Subtract the volume of ferrocyanide solution used in this titration from that used in titrating the zinc solution. Calculate the weight of zinc equivalent to the zinc oxide weighed out and divide by the volume (corrected) of ferrocyanide solution used.

#### IV. Outline of Method for Determination of Zinc in an Ore Which Contains Neither Copper nor Cadmium

**Decomposition.** Weigh out 1.5 grams of the finely ground sample into a 200-cc. beaker, add 10 cc. of concentrated hydrochloric acid, cover with a watch glass and warm gently until violent action ceases and hydrogen sulfide is no longer given off. Add 5 cc. of dilute nitric acid and again warm to insure complete decomposition of pyrite, which might otherwise retain some zinc, and also to effect complete oxidation of all the iron present. After violent action ceases remove the watch glass and evaporate almost to complete dryness, but avoid a temperature in excess of 100°.

**Separation of the Zinc.** Add to the residue 10 cc. of concentrated hydrochloric acid, slowly heat to the boiling point and then add 50 cc. of water. Heat the solution to the boiling point, add 10 cc. of bromine water and then a moderate excess of ammonium hydroxide and keep near the boiling point for about five minutes. Allow the precipitate of iron, manganese and gangue-matter to settle, then filter through a small filter receiving the filtrate into a 250-cc. graduated flask, allow to drain and wash four times with 10 cc. portions of water. Replace the graduated flask by the



beaker just emptied and pour over the filter sufficient warm dilute hydrochloric acid to change all of the ferric hydroxide into ferric chloride, then wash the filter free from iron. Dilute the solution in the beaker to at least 50 cc., heat to boiling and again precipitate with ammonium hydroxide and bromine water; filter and wash as before, receiving the filtrate in the graduated flask previously used. Add sufficient hydrochloric acid to this solution to make it slightly acid.

**Division of Zinc Solution.** Cool the solution in the flask to the temperature of the room and dilute with water until the liquid reaches the mark on the neck of the flask. Place a stopper in the neck of the flask and mix its contents thoroughly by inverting the flask and shaking vigorously several times. Rinse out a 50-cc. pipette with some of the zinc solution and discard the solution thus used; then measure out two 50-cc. portions of the solution into 400-cc. beakers.

**Titration of Zinc.** Add to each of the 50-cc. portions of zinc solution 5 cc. of concentrated hydrochloric acid and dilute to 200 cc. Heat one of these solutions to 80° C. and titrate with the ferrocyanide solution adding 10 cc. before making the first test and then 1-cc. portions successively until an end point is reached. Heat the second zinc solution to 80° C. and titrate with the ferrocyanide solution, adding 1 cc. less than the total amount used in the previous titration before making the first test and then 0.1-cc. portions successively until an end point is reached. Calculate the percentage of zinc present.

## V. Questions and Problems. Series 23

1. What is the replacing power and the normal value of potassium ferrocyanide, when used to determine zinc by the reaction given on page 297?

2. In titrating a solution which has a volume of 200 cc. and contains 0.150 gram of zinc 30 cc. of ferrocyanide solution are required to precipitate the zinc and 0.5 cc. to give an end point with the solution; if 20.5 cc. are added before any tests are made with the indicator and then a test is made (necessitating the removal of 0.04 cc.) after each successive addition of 1-cc. portion of solution, how large a volume of ferrocyanide solution would be required for the titration?

3. Should the delicacy with which the end point is recognized be affected

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by the size of the drop removed for the test, assuming the volume of indicator used is not changed?

4. Explain the action of ammonium hydroxide and ammonium chloride in the separation of iron from zinc. Could any other reagent be substituted (*a*) for ammonium hydroxide (*b*) for ammonium chloride?

5. Outline a method for the determination of zinc in an ore which also contains copper and cadmium.

## SECTION VIII

### CHAPTER XXXI

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#### GENERAL THEORY OF ACIDIMETRY AND ALKALIMETRY

##### I. General Theory of Neutralization Processes

**Completeness of Reactions Involving Neutralization.** Many processes which depend upon the use of a standard solution of an acid or base are in use. The most important of these involve simple neutralization. As shown on page 70, the equilibrium constant of such reactions can be calculated by dividing the product of the dissociation constants of the acid and base by that of water, and therefore such reactions are made most complete when the acid or base used for the standard solution is strong. If it is assumed that the dissociation constant of the acid or base used is one, the equilibrium constant of the reaction is simply the dissociation constant of the acid or base being titrated divided by  $1 \times 10^{-14}$ .

**Composition of Mixtures Titrated at the True End Points.** The true end points of these determinations correspond to that stage of the titration at which equivalent amounts of acid and base are present. The actual value of  $(H^+)$  at the true end point can be calculated from the equilibrium constant of the reaction, but since such reactions are nearly complete it is preferable to calculate it from the constant representing the reverse process, namely, the hydrolysis of the salt formed. Salts which yield a strong anion and a strong cation are hydrolyzed to a negligible degree only, and therefore  $(H^+) = 1 \times 10^{-7}$  at the true end point in all titrations between strong acids and strong bases. The hydrolysis of salts, which yield an anion and a cation which are equally weak,

is larger, but since in such cases the ability of the cation to increase  $(H^+)$  is offset by the ability of the anion to increase  $(OH^-)$ ,  $(H^+) = 1 \times 10^{-7}$  in all concentrations of such salts. Hence in titrations between acids and bases which have the same dissociation constants  $(H^+) = 1 \times 10^{-7}$  at the true end points. The hydrolysis of salts which yield a weak anion and a strong cation gives solutions in which  $(H^+)$  is less than  $1 \times 10^{-7}$ , but, if the anion is strong and the cation weak,  $(H^+)$  is greater than  $1 \times 10^{-7}$ . The exact value of  $(H^+)$  at the true end points, in which such salts are found, depends upon the total concentration of the salt present and upon the hydrolysis constant. The hydrolysis constant of the salt derived from a strong base and an acid whose constant is  $1 \times 10^{-4}$  is  $1 \times 10^{-10}$ . The value of  $(OH^-)$  in a 0.025 N solution of such a salt would equal  $\sqrt{.025 \times 10^{-10}}$  or  $1.58 \times 10^{-6}$  and of  $(H^+)$  would equal  $6.3 \times 10^{-9}$ . These values would also characterize the solution at the true end point when 25 cc. of the acid whose concentration is 0.1 N is titrated with the base of the same concentration if the final volume is made 100 cc. In like manner the titration of acids whose constants are  $1 \times 10^{-2}$ ,  $1 \times 10^{-6}$ , and  $1 \times 10^{-8}$  would yield mixtures in which  $(H^+)$  would equal  $6.3 \times 10^{-8}$ ,  $6.3 \times 10^{-10}$  and  $6.3 \times 10^{-11}$  respectively. Similarly it can be calculated that, in the titration of a series of bases whose dissociation constants are  $1 \times 10^{-2}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-6}$  and  $1 \times 10^{-8}$ ,  $(H^+)$  at the true end-points would equal  $1.58 \times 10^{-7}$ ,  $1.58 \times 10^{-6}$ ,  $1.58 \times 10^{-5}$  and  $1.58 \times 10^{-4}$  respectively. These facts emphasize the need of making use of indicators of varying degrees of sensibility toward  $(H^+)$  in titrating acids and bases.

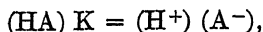
**Buffer Effects.** If an acid is added to a solution containing a moderate concentration of a weak anion, some of the  $H^+$  added will unite with the anion and reduce the increase in  $(H^+)$  which should have taken place. Similarly, if a base is added to a solution which contains a weak cation, some of the  $OH^-$  will unite with the cation and reduce the increase in  $(OH^-)$  which should have taken place. The rates of change in the values of  $(H^+)$  or  $(OH^-)$  resulting from the addition of acids or bases to solutions of salts may therefore be very different from the rates when added to water. If sodium hydroxide or hydrochloric acid is added to a

solution of sodium chloride, practically all the  $H^+$  or  $OH^-$  added goes to increase the  $(H^+)$  or  $(OH^-)$  already present, as in pure water. If these reagents are added to solutions containing ammonium acetate, the  $NH_4^+$  takes up some of the  $OH^-$  or the  $C_2H_3O_2^-$  takes up some of the  $H^+$ , and this salt buffers the solution for both bases and acids. The effect increases with an increase in the concentration of the salt present and the weakness of the ions which the salt forms. As the end point is approached in titrating an acid with a base the concentration of the salt becomes relatively large, and, if the salt yields a weak anion or a weak cation, it acts as a buffer. In the titration of a strong acid with a strong base therefore  $(H^+)$  must decrease more rapidly as the true end point is approached than when a weak acid is titrated with a weak base, not only because the fraction of base added, which is ionized, is small, but also because some of it is buffered by the salt present. Similar differences in the rate of change in  $(H^+)$  in the two titrations appear as the titration is carried beyond the true end point. Buffer effects also arise as the end points are approached in the titration of weak acids with a strong base or weak bases with a strong acid.

**Rate of Change in  $(H^+)$  in Neutralization Processes.** The actual change in  $(H^+)$  during neutralization must conform to the requirement  $(H^+) \times (OH^-) = 1 \times 10^{-14}$ , and therefore is analogous to the change in  $(R^+)$  when titrated with  $(A^-)$ , with which it forms a slightly soluble salt, as discussed in Chapter XXVII. The actual rate of change can be calculated if certain simplifying assumptions are made. It will be assumed first that 25 cc. of 0.1 N acid is titrated with 0.1 N base, that the final volume is 100 cc. and that both acid and base are strong. Obviously when 25 cc. of base have been added  $(H^+) = (OH^-) = 1 \times 10^{-7}$ . If only 20 cc. have been added the mixture is the same as a solution in which the salt concentration is 0.02 and the acid concentration is 0.005. Since the hydrolysis of the salt is negligible and the acid is practically completely dissociated,  $(H^+) = 5 \times 10^{-3}$ . If the acid titrated is weak and the base strong, the calculation is not so simple because the weak anion acts as a buffer or, expressed differently, decreases  $(H^+)$  by its hydrolysis. If 24.5 cc. of base have been added and the dissociation constant of the acid is

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$1 \times 10^{-8}$ , the total concentration of salt is 0.0245 and that of free acid is 0.0005. If we use  $x$  to represent the actual value of  $(H^+)$ , then  $(0.0005 - x)$  represents undissociated acid and  $(.0245 + x)$  the weak anion. Substituting in the expression,



we get

$$(0.0005 - x) (1 \times 10^{-8}) = (0.0245 + x)x$$

When this quadratic equation is solved we find that  $x = 2 \times 10^{-10}$ . Similarly, after 25.5 cc. of base have been added the total concentration of base is 0.0005 and that of salt is 0.025. If  $x$  represents the fraction of salt, or anion from the salt, hydrolyzed,  $0.025x$  must represent the resulting  $(OH^-)$  and  $(0.0005 + 0.025x)$  the total  $(OH^-)$ . Also,  $0.025x$  must represent the  $(HA)$  formed and  $(1 - x)0.025$  the anion left unhydrolyzed. The hydrolysis constant has the value  $1 \times 10^{-6}$  and therefore

$$(A^-) \cdot (1 \times 10^{-6}) = (OH^-)(HA),$$

or,

$$(1 - x)0.025 \cdot (1 \times 10)^{-6} = (0.0005 + 0.025x)(0.025x).$$

When this quadratic equation is solved for  $x$ , the value  $1.78 \times 10^{-3}$  is found, and therefore  $0.025x = 4.45 \times 10^{-5}$ . Hence  $(OH^-) = (0.0005 + 0.025x)$ , or  $5.4 \times 10^{-4}$ , and  $(H^+) = 1.8 \times 10^{-11}$ .

By the use of these procedures the changes in  $(H^+)$  during the titration of acids whose constants are  $1 \times 10^{-2}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-6}$ , and  $1 \times 10^{-8}$  with a strong base, between the stages corresponding to 80 per cent (20 cc.) and 120 per cent (30 cc.) neutralization, have been calculated. The results are represented by the four graphs of Fig. 54. They present striking resemblances to those of Fig. 49 and clearly show that the difficulty of choosing effective methods of reducing the error involved in determining the end points of the titration to negligible values increases as the strength of the acid titrated decreases. The error involved in finding the end point, when the strongest of the four acids is titrated, by the use of an indicator which shows a color change

when  $(H^+)$  ranges anywhere between about  $1 \times 10^{-6}$  and  $1 \times 10^{-10}$ , should not exceed 0.1 cc. or one part in 250. If the weakest of the four acids is titrated, the possible range of variation in  $(H^+)$  at which the color change takes place would be about  $6.5 \times 10^{-11}$  to  $4.5 \times 10^{-11}$  for the same degree of accuracy. Decreasing the total volume of the mixture titrated or increasing

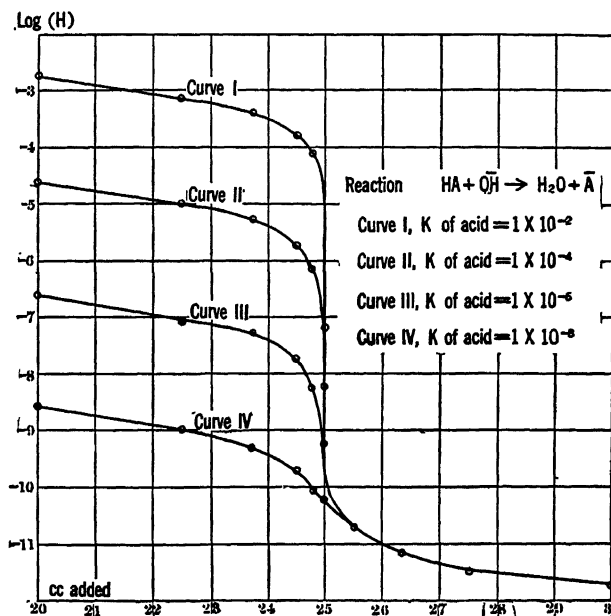


Fig. 54.—Showing changes in  $(H^+)$  during the titration of 25 cc. of 0.1 N HA with 0.1 N NaOH.

the concentration of the titrating solution would increase these ranges somewhat as shown on page 262.

The data for the graphs representing the titration of weak bases with a strong acid can be calculated in like manner. If it be assumed that the ordinates represent  $(OH^-)$  instead of  $(H^+)$ , those of Fig. 54 also represent the changes in  $(OH^-)$  when bases whose constants are  $1 \times 10^{-2}$ ,  $1 \times 10^{-4}$ ,  $1 \times 10^{-6}$ , and  $1 \times 10^{-8}$

are titrated with a strong acid, assuming the same total volume and concentration of the titrating solution.

## ✓ II. General Theory of Displacement Processes

**Completeness of Reactions Involving Displacement.** A second series of processes, which makes use of standard acids and bases as titrating solutions, involves displacement of a weak acid by a strong acid, or of a weak base by a strong base, from their salts. It has been shown on page 68 that the equilibrium constants for such reactions can be calculated by dividing the dissociation constant of the strong acid or base used by that of the weak acid or base liberated. Since the dissociation constants of the strongest acids available do not exceed one, the equilibrium constants of such reactions are not large enough to insure a satisfactory degree of completeness unless the dissociation constants of the weak acid or base formed are very small. Certain of these reactions involve the formation of slightly soluble gases such as carbon dioxide and hydrogen cyanide, which greatly increases their completeness, especially if the process is carried out at a temperature at which the solubility of the resulting gas is very small.

**Composition of Mixtures Titrated at the True End Points.** The true end points of such processes represent that stage of the titration at which the number of equivalents of strong acid or base added equals the number of equivalents of salt present. Since only those reactions which are nearly complete need be considered, it is easier to calculate ( $H^+$ ) at the true end points by assuming that the composition of the mixture is identical with that of a mixture composed of the new salt formed and the weak acid or base formed by displacement. If, for example, the attempt is made to titrate sodium acetate with hydrochloric acid, the end point mixture equals that of the proper amounts of sodium chloride and acetic acid. Since the sodium chloride yields a strong anion and a strong cation, hydrolysis may be neglected, and it is only necessary to calculate ( $H^+$ ) due to dissociation of the acetic acid. If 25 cc. of a 0.1 N solution of a sodium salt of an acid whose constant is  $1 \times 10^{-6}$  is titrated with a strong acid, and the total



volume is 100 cc., the total concentration of the displaced acid must be 0.025 and, therefore, according to the usual procedure,

$$(\text{H}^+) = \sqrt{0.025 \times (1 \times 10^{-6})} = 1.58 \times 10^{-4}.$$

Similarly, if the constant for the titrated acid is  $1 \times 10^{-4}$ , then  $(\text{H}^+)$  equals  $1.58 \times 10^{-3}$ , and if it is  $1 \times 10^{-8}$ ,  $(\text{H}^+)$  becomes  $1.58 \times 10^{-5}$ . The value of  $(\text{H}^+)$  at the true end point therefore decreases at a uniform rate with decreasing strength of the displaced acid.

**Rate of Change in  $(\text{H}^+)$  in Displacement Processes.** The change in  $(\text{H}^+)$  during such titrations must also conform to the requirement that  $(\text{H}^+) \times (\text{OH}^-) = 1 \times 10^{-14}$ . The calculation of  $(\text{H}^+)$  at any stage of the titration is easily performed if simplifying assumptions are made. It will first be assumed that 25 cc. of a 0.1 N solution of a sodium salt of an acid HY, whose constant is  $1 \times 10^{-8}$  is titrated with a 0.1 N solution of a strong acid, HX, and that the final volume is 100 cc. After 20 cc. of acid have been added the total concentration of displaced weak acid, HY is 0.02, and that of the original salt, NaY, still left is 0.005. If  $x$  represents  $(\text{H}^+)$ , the displaced acid left unionized must be  $(0.02 - x)$  and that of the salt or anion,  $\text{Y}^-$ , present must equal  $(0.005 + x)$ . Since

$$\text{HY} \cdot K = (\text{H}^+)(\text{Y}^-),$$

then

$$(0.02 - x)(1 \times 10^{-8}) = x(0.005 + x)$$

When this quadratic equation is solved for  $x$  the value  $4 \times 10^{-8}$  is found.

After an excess of the strong acid has been added the mixture can be assumed to consist of the salt NaX, which is not appreciably hydrolyzed, the displaced acid HY, and the strong acid HX in excess. In order to calculate  $(\text{H}^+)$  due to both acids it will be assumed that all the strong acid HX is completely dissociated and that the fraction of HY which is dissociated is represented by  $x$ . After 25.5 cc. of strong acid have been added, the total

concentration of displaced acid becomes 0.025 and the strong acid in excess must equal 0.0005. Hence,

$$(\text{H}^+) = (0.0005 + 0.025x),$$

also

$$0.025x = (\text{Y}^-),$$

and

$$(1 - x)(0.025) = (\text{HY}).$$

Since

$$(\text{HY}) \cdot K = (\text{H}^+) \cdot (\text{Y}^-),$$

then

$$(1 - x)(0.025)K = (0.0005 + 0.025x)(0.025x).$$

When solved for  $x$  this equation gives the value  $2 \times 10^{-5}$  and therefore

$$0.025x = 5 \times 10^{-7},$$

and

$$(\text{H}^+) = 0.0005002 \quad \text{or} \quad 5 \times 10^{-4}.$$

Further calculations of the change in  $(\text{H}^+)$  during the titration of sodium salts of acids whose constants are  $1 \times 10^{-4}$ ,  $1 \times 10^{-8}$ , and  $1 \times 10^{-12}$  are plotted as graphs in Fig. 55. They clearly show, as would be anticipated, that the rate of change in  $(\text{H}^+)$  at the true end point is very large in the graph representing the salt of the weakest acid and decreases progressively in those representing the titration of salts of stronger acids.

### III. General Theory of Indicators Used

**Chemical Behavior.** The substances used as indicators in titrations involving neutralization or displacement are all organic compounds which have the properties of weak acids, or weak bases, or both. The behavior of one of the simplest, namely para-nitro-phenol, will be considered in some detail. The hydroxyl group of this indicator has acidic properties, and it forms well-defined salts with strong bases. When added to water or to solutions in which  $(\text{H}^+)$  is large, it is but slightly dissociated, but, if  $(\text{H}^+)$  is made small by the addition of a slight excess of a base, it

undergoes almost complete dissociation. The solutions in which this occurs change from colorless to light yellow, which change might be attributed to changes in the degree of dissociation. It is known, however, that most of the organic compounds which possess an intense colorific power contain a "chromophore group." Para-nitro-phenol does not contain such a group, but if it is

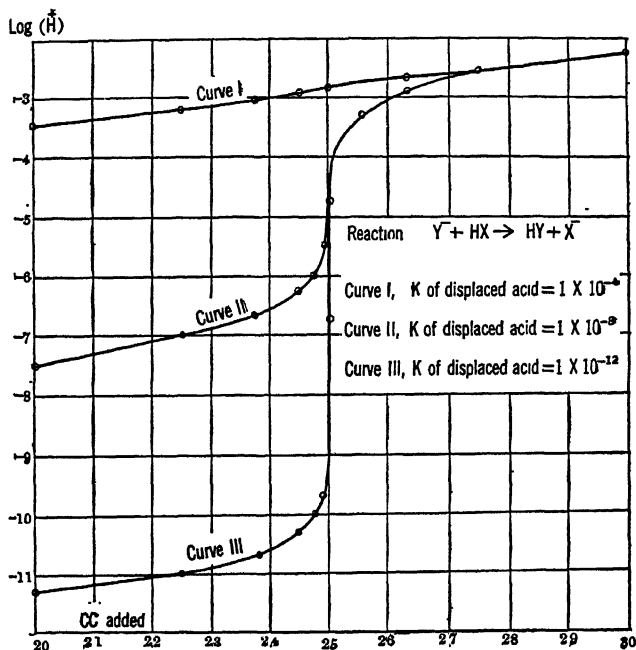


Fig. 55.—Showing changes in ( $H^+$ ) during the titration of 25 cc. of 0.1 N NaS with 0.1 N HX.

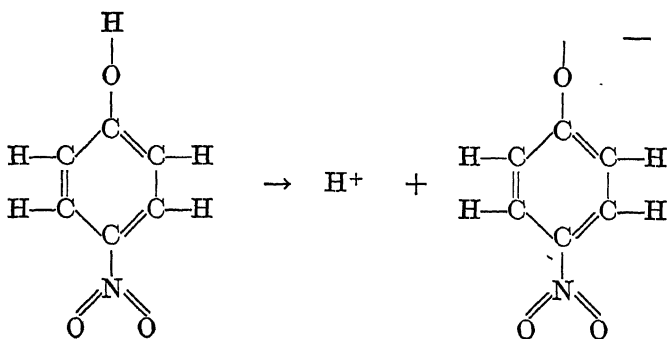
assumed that the hydrogen of the hydroxyl group readily shifts its position and becomes attached to one of the oxygen atoms of the nitro groups, the resulting compound contains the chromophore group  $=C_4H_4=$  or acquires a quinoid instead of a benzenoid structure. Since similar changes have been shown to take place in a number of other indicators, it is probable that it takes place in para-nitro-phenol. If so, the color of solutions containing it is

determined by the sum of the concentrations of the quinoid form of the free acid, the anion, and the salt. It is easy to show, however, that there is no further color change after a bare excess of alkali has been added, and it is probable that in such solutions practically all of the indicator is in the form of the quinoid anion since the salt should be largely dissociated and very little of the undissociated acid should be left. We may assume, therefore, that the essential feature of the color change is the conversion of undissociated benzenoid acid into quinoid anion. If we make this assumption we may also assume the following mechanism:

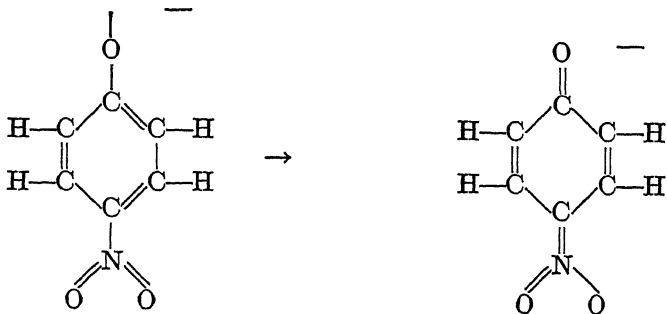
- (a) benzenoid acid  $\rightarrow$  benzenoid ion + hydrogen ion,  
 (b) benzenoid ion  $\rightarrow$  quinoid ion.

This may be represented by

(a)



(b)



Since the formation of the color represents the sum of the two processes, the equilibrium constant which determines the formation of color must equal the product of the constants which determine the two equilibria, that is,

$$K_I = K_a \cdot K_b = (H^+) \cdot \frac{(O=C_6H_4=NO-O)^-}{(HO-C_6H_4-NO_2)},$$

in which  $K_I$  is the "indicator constant,"  $K_a$  the dissociation constant of the benzenoid form, and  $K_b$  the tautomeric transformation constant. The evaluation of the indicator constant involves the measurement of the ratio between the colored and the uncolored forms of the indicator in a solution in which  $(H^+)$  is known. If the fraction of indicator in the colored form is represented by  $x$ , the preceding equation becomes

$$K_I = (H^+) \frac{x}{(1-x)}$$

We might also have assumed a second mechanism, namely,

- (a) benzenoid acid  $\rightarrow$  quinoid acid,
- (b) quinoid acid  $\rightarrow$  quinoid ion + hydrogen ion.

This would have led to an expression for the indicator constant whose value is determined by the product of two other constants, namely, the transformation constant of the benzenoid acid and the dissociation constant of the quinoid acid, and the concentration of hydrogen ion. The evaluation of this constant is also possible if the ratio between the colored and uncolored forms of the indicator in the presence of a known concentration of hydrogen ion has been ascertained. This leads to exactly the same result as the former mechanism.

The preceding expression for the indicator constant may be considered to be purely empirical. Its theoretical derivation involves several simplifying assumptions, but the fact that it has been found to express with a fair degree of accuracy the behavior of a number of indicators justifies its use.

**Determination of Indicator Constant.** The determination of  $K_I$  of a one-color indicator such as para-nitro-phenol is easily made by using two color comparison tubes as *A* and *B* of Fig. 56.

Let it be assumed that *A* contains a solution in which ( $H^+$ ) is known, and *B* a solution in which ( $H^+$ ) is so small that all the indicator can be assumed to be in the quinoid form; also, that when viewed against a white background the two solutions show

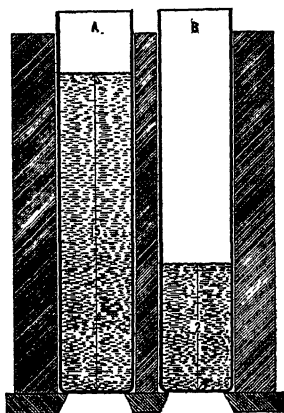


Fig. 56.—Illustrating a method of determining the value of an indicator constant

equal color absorption when the thickness of the layer of solution in *A* is related to that of the solution in *B* as 5 is to 2. If *a* represent the total concentration of indicator in both cylinders, and *x* the fraction of it in *A* in the quinoid form, *ax* must represent the concentration of the quinoid form in *A*, and therefore  $5ax = 2a$ ,  $x = \frac{2}{5}$  and  $(1 - x) = \frac{3}{5}$ . By substituting in the preceding expression we find

$$K = (H^+) \frac{2}{3}.$$

By analogy, the constant for indicators which are mono-acid bases should be defined by the expression

$$K = (OH^-) \cdot \frac{x}{1 - x},$$

in which *x* is the fraction of the indicator in one of its two colored forms. Since ( $OH^-$ ) must always equal  $1 \times 10^{-14} \div (H^+)$ , the expression may be written

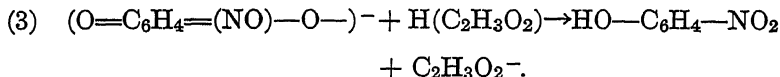
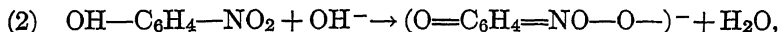
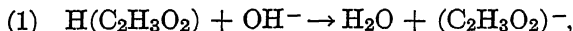
$$K = \frac{1 \times 10^{-14}}{(H^+)} \cdot \frac{x}{(1 - x)}.$$

Therefore the constants of basic indicators may be defined in the same terms as those used to define acidic indicators. In the experimental determination of the indicator constant, it is not necessary to know whether it is an acid or a base.

The reactions of many indicators are more involved than those of para-nitro-phenol. Some are colored in acid and colorless in basic solutions; some show two different colors and probably involve transformation of one chromophore containing molecular

species to another containing a different chromophore; and some dissociate in two stages, with the color change depending upon two dissociation constants.

**Changes of an Indicator During a Titration.** The form of the indicator constant expression shows that the value of  $(H^+)$  at which its color changes, is large in proportion as the value of  $K_I$  is large, and these values suggest at once the kinds of titrations for which each indicator is adapted. It is also possible to calculate the specific value of  $K_I$  which the indicator used in a specific determination should have in order to give the best results possible in that titration. We will consider two simple titrations. First, let it be assumed that acetic acid is being titrated with sodium hydroxide and that para-nitro-phenol is used as indicator. There are three reactions concerned in this titration, namely:

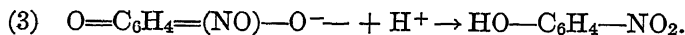
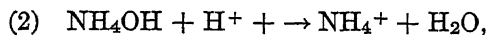
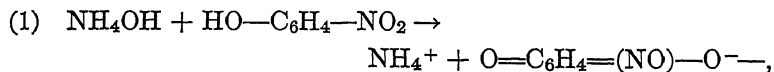


The accuracy depends upon the extent to which (1) is complete before (2) begins to take place, and also upon the promptness with which (2) takes place after (1) has been completed. Reaction (3) which expresses the preponderance of (1) over (2) assures the disappearance of any color which the solution may have acquired during the earlier stage of the titration owing to incomplete stirring. The process corresponds to the first of the two cases discussed in Chapter XXVII. Since reaction (1) involves simple neutralization, its constant can be calculated by dividing the dissociation constant of acetic acid,  $1.8 \times 10^{-5}$ , times the dissociation constant of potassium hydroxide, 1, by the dissociation constant of water. This gives  $1.8 \times 10^9$ . Reaction (2) involves both neutralization and a tautomeric change, but it can be shown, by the same procedure as was used in determining the value of the neutralization constant (see page 71), that its equilibrium constant equals the product of the indicator constant,  $1 \times 10^{-7}$ , and that of potas-

sium hydroxide, 1, divided by the dissociation constant of water. Its value therefore is  $1 \times 10^7$ . Reaction (3) involves both displacement and tautomeric change, but its constant equals that of the indicator divided by that of acetic acid, and has the value  $1.8 \times 10^2$ . These figures clearly suggest the probability of a premature end point, and experience in the use of this indicator confirms the prediction. The best indicator for the titration, one in which the probability of a premature and deferred end point would be equal, would be one which gives the same constant for both (2) and (3), namely  $4.2 \times 10^{-10}$ . A further study of these reactions will show that the indicator used in the titration of acids should have a constant whose value is large compared with the dissociation constant of water, but small compared with that of the acid being titrated.

Since para-nitro-phenol is a one-color indicator, there is no objection to using large concentrations of it in order to favor the reactions in which it takes part. This is not true of a two-color indicator since large concentrations of either form mask the color change. The use of small amounts of para-nitro-phenol in the illustration given would reduce the probability of a premature end point.

In the titration of ammonium hydroxide with hydrochloric acid, using para-nitro-phenol, the three equilibria are:



The process corresponds to the second of the two classes of titrations discussed in Chapter XXVII. Its accuracy depends upon the completion of (2) before (3) begins to take place. The equilibrium constant for (1) is  $(1.8 \times 10^{-5})(1 \times 10^{-7}) \div 1 \times 10^{-14}$  or  $1.8 \times 10^2$ ; for (2) it is  $(1.8 \times 10^{-5}) \times 1 \div 1 \times 10^{-14}$  or  $1.8 \times 10^9$ , and for (3) it is  $1 \div 1 \times 10^{-7}$  or  $1 \times 10^7$ . Obviously here also there is larger probability of a premature than a deferred



end point. The use of an indicator whose constant is  $2.4 \times 10^{-5}$  would make the two possibilities equally probable.

A study of the three reactions makes it clear that in the titration of bases an indicator whose constant is large in proportion as the dissociation constant of the base is small, but small as compared with that of the acid used, should be employed.

**The Transition Interval.** Although the colorific intensity of the substances used as indicators is large, and the amount required to impart a sufficient intensity of color to the titrating solution is usually less than a milligram, the rate at which the color changes from that of one form to that of the other is gradual rather than abrupt unless concentrated solutions are used. With every indicator there is a particular value of  $(H^+)$  at which the change may be said to begin, and another at which it may be called complete. The difference between these values is called the "transition interval." Although the identification of the transition interval depends upon the judgment and experience of the experimenter, and is therefore far from exact, it may be used with more assurance and ease than the indicator constant in fixing the particular titrations to which an indicator is adapted. With many of the one-color indicators, the color shades which characterize the transition interval are fairly uniform, but, especially with the two-color indicators, owing to differences in the nature of these colors and their relative colorific intensities, there are certain stages at which the color change is most abrupt. Obviously those indicators which have small transition intervals, or which exhibit some particular point at which the change is very abrupt, can be used with the greatest ease and accuracy.

**Methods of Using Indicators.** It has been shown in Sections I and II of this chapter that many of the titrations involving neutralization and displacement are characterized by a very rapid rate of change in  $(H^+)$  at the true end point. For such titrations little care need be exercised either in choosing the indicator, or in fixing upon the particular color shade to which the titration should be carried. With other titrations it becomes necessary not only to choose an indicator whose transition interval includes the particular value of  $(H^+)$  which characterizes the true end point but also to carry the titration to a specific color shade.

The description and definition of color shades presents many difficulties and it is scarcely possible to keep such characters in mind after they have been observed. It becomes necessary to prepare a color standard with which the solution being titrated can be compared during the progress of the titration. Such a standard should contain the same concentration of indicator as the solution being titrated and have also the particular ( $H^+$ ) which characterizes the true end point. It is often necessary to determine the value of ( $H^+$ ) actually present in an unknown solution rather than the total available acid. Such a procedure must be based upon a method which does not use up ( $H^+$ ). It can be done, at least for solutions in which ( $H^+$ ) does not exceed certain limits, by making use of a series of color standards, containing the same concentrations of the indicator associated with different concentrations of ( $H^+$ ). The standards are retained in cylindrical tubes of uniform diameter, and the color of the unknown solution, in a tube of the same form, is compared with different members of the series until the one which most nearly matches it is found. The preparation of solutions containing known concentrations of ( $H^+$ ) is best accomplished by diluting strong hydrochloric acid to the degree demanded by the known values of its activity as given on page 78, or, still better, by the use of combinations of a certain weak acids and their salts whose ( $H^+$ ) values have been established by measurement with the hydrogen electrode. Solutions of soluble phosphates and phthalates are especially useful, and, since such solutions are buffered, less care need be exercised in preparing them.

✓ **Classification of Indicators.** The most useful classification of indicators is based upon their transition intervals. Such a classification ignores the actual nature of the changes they undergo, but shows at once the particular portion of the ( $H^+$ ) scale for which they can be used. Only a limited number are needed to include the entire range of ( $H^+$ ) which can be identified by means of indicators. Individual experience enters largely into the selection of such a series but the following have many desirable features.<sup>1</sup>

<sup>1</sup> The data upon which this list is based are taken from the summaries given by Clark, "The Determination of Hydrogen Ion," pages 41 and 67 (1920).

Methyl orange is the sodium salt of dimethyl-amino-azo-benzene-sulfonic acid. The indicator solution is prepared by dissolving 1 gram of the salt in water and diluting to 1 liter. Not more than 2 drops should be used for each 100 cc. of solution titrated. Added to water it gives a lemon-yellow color, which is not changed by adding  $\text{OH}^-$ , but, if  $\text{H}^+$  is added, a clearly defined change to salmon color appears when  $(\text{H}^+)$  becomes  $4 \times 10^{-5}$ , and this gradually changes to red when  $(\text{H}^+)$  becomes  $8 \times 10^{-4}$ . Methyl orange is especially useful in the titration of weak bases or the salts of weak acids.

Methyl red is dimethyl-amino-azo-benzene-ortho-carboxylic acid. The indicator solution is prepared by dissolving 1 gram of this substance in a liter of 90 per cent alcohol. From 2 to 4 drops per 100 cc. should be used. It changes fairly uniformly from pink to yellow as  $(\text{H}^+)$  changes from  $4 \times 10^{-5}$  to  $1 \times 10^{-6}$ .

Para-nitro-phenol solution is prepared by dissolving 1 gram of para-nitro-phenol in a liter of 50 per cent alcohol. One drop is sufficient to give a satisfactory color to 100 cc., but there is no objection to using as many as 10 drops for certain titrations. This indicator changes from colorless when  $(\text{H}^+)$  is  $1 \times 10^{-5}$  to yellow when  $(\text{H}^+)$  is  $1 \times 10^{-7}$ .

Brom-thymol-blue is di-bromo-thymol-sulfon-phthalein. The indicator solution is prepared by dissolving 1 gram in a liter of 95 per cent alcohol. One drop is usually sufficient for 100 cc. Solutions in which  $(\text{H}^+)$  is greater than  $1 \times 10^{-6}$  are yellow, and change to yellow-green when  $(\text{H}^+)$  is  $1 \times 10^{-7}$  and to deep blue when  $(\text{H}^+)$  is  $2 \times 10^{-7}$ .

Phenol red is phenol-sulfon-phthalein. The indicator solution is composed of 1 gram of phenol red per liter of 95 per cent alcohol. One drop is used for a titration. Solutions in which  $(\text{H}^+)$  is  $2.2 \times 10^{-7}$  are yellow, but become red when  $(\text{H}^+)$  reaches  $6 \times 10^{-9}$ .

Rosolic acid, or aurine, is a derivative of tri-phenyl-methane. The indicator solution should contain 1 gram in a liter of 50 per cent alcohol. One or two drops should be used for 100 cc. Solutions in which  $(\text{H}^+)$  is  $1.2 \times 10^{-7}$  are yellow but become red when  $(\text{H}^+)$  is  $1 \times 10^{-8}$ .

Phenolphthalein solution is made by dissolving 1 gram in a

liter of 50 per cent alcohol. One drop of this solution is sufficient for most titrations, but more are often used. It remains colorless if  $(H^+)$  is greater than  $1 \times 10^{-8}$  but becomes red when  $(H^+)$  becomes  $1 \times 10^{-10}$ . Phenolphthalein is especially useful in the titration of weak acids.

#### IV. The Use of Electromotive Force Measurements

**Determination of End Points.** Although the end points of a very large number of determinations are easily and correctly found by the use of indicators, the error of the method increases in proportion as the inflection of the titration curve at the end point decreases. The inflection of many titration curves is so slight that the results based upon such titrations, when indicators are used, are only roughly quantitative, and may be worthless. In certain cases it becomes necessary to titrate solutions which contain colored compounds, or precipitates, or substances which act as buffers. These greatly modify the character of the color change of the indicator used.

It has been shown on page 158 that the electromotive force of a cell, one electrode of which is a hydrogen electrode, depends upon the value of  $(H^+)$  in the solution surrounding that electrode. If the potential due to the other electrode is known, that due to the hydrogen electrode can be found by adding or subtracting its value from the electromotive force of the combination, and the value of  $(H^+)$  can then be calculated from a simple formula. If, for example, the second electrode is a normal calomel electrode, mercury in contact with a normal solution of potassium chloride saturated with calomel, the calculation is made by substituting in the expression:

$$\text{Cell voltage} = 0.286 - .059 \log (H^+),$$

in which it is assumed that the hydrogen gas supplied to the hydrogen electrode is at atmospheric pressure. This formula shows that a simple linear relation must exist between the electromotive force of the cell and the value of  $\log (H^+)$ . Owing to the very great degree of accuracy with which electromotive force measurements can be made, the value of  $(H^+)$  can be deter-

mined much more accurately in this manner than by the use of indicators. Such measurements can be carried out in various ways. First, the titration may be carried to the point at which the electromotive force found corresponds to that value of  $(H^+)$  which has been calculated to represent the true end point of the titration or which equals that of a comparison solution, whose composition has been made the same as that which the solution being titrated should have at the true end point. Second, the titration may be carried beyond the true end point and the point at which the electromotive force shows the maximum rate of change found, usually by plotting the voltage against the volume of titrating solution used.

**Standardization of Procedure.** It will be recalled that most of the calculations relating to changes in  $(H^+)$  during a titration involve simplifying assumptions, and therefore give approximate results only. Measurements of  $(H^+)$  by the hydrogen electrode give values for the actual activities with a high degree of accuracy. The form of the titration curve found by electromotive force measurements furnish the only entirely reliable data by means of which the proper conditions for a titration can be specified. Large numbers of such curves have been determined and should be made use of.<sup>1</sup>

## V. Summary of the Methods of Acidimetry and Alkalimetry

**Titration of Monobasic Acids.** The facts presented in the preceding sections of this chapter show that strong acids can be accurately titrated with a strong base by using any of the indicators there listed, or by employing a hydrogen electrode for the determination of the end point. The titration of a weak acid cannot be undertaken intelligently unless the value of its dissociation constant, many of which are given on page 74, is known. Knowing this value, it is possible to calculate the value of  $(H^+)$  at the true end point, and also to estimate roughly, by reference to the graphs of Fig. 54, the inflection of the titration curve. It is then desirable to choose as the best indicator, that one whose transition

<sup>1</sup> See especially the extensive bibliography in Clark's "Determination of the Hydrogen Ion" (1920) and Prideaux's "Theory and Use of Indicators" (1917).

interval includes that portion of the titration curve which shows the most rapid rate of change in  $(H^+)$ . Reducing the volume of the solution titrated and increasing the strength of the titrating solution increases the accuracy of the process. Satisfactory results can be obtained in titrating acids, whose constants are not less than  $1 \times 10^{-7}$ , without special precautions. In titrating still weaker acids, it is necessary to use a prepared color standard, representing the exact shade of color the solution should have at the true end point as a standard of comparison, or to employ the hydrogen electrode.

**Titration of Di- and Tri-basic Acids.** The theory of the titration of these acids is more complex, since neutralization takes place in stages, and the completeness of each stage is determined by different constants. Thus, in the titration of orthophosphoric acid, the value of  $(H^+)$  is determined for the most part by the first dissociation constant,  $1.1 \times 10^{-2}$ , up to the point at which one equivalent of base has been added, by the second constant,  $2 \times 10^{-7}$ , up to the point at which two equivalents have been added, and by the third,  $4 \times 10^{-13}$ , up to the point at which three equivalents have been added. The value of  $(H^+)$  at the end of the first stage should equal that of a solution of monosodium phosphate,  $NaH_2PO_4$ . If this salt is dissolved in water, the further ionization of  $H_2PO_4^-$  into  $H^+$  and  $HPO_4^{--}$  is determined by the constant  $2 \times 10^{-7}$  and its hydrolysis by the constant  $1 \times 10^{-14} \div 1.1 \times 10^{-2}$ . The net effect is a relatively large increase in  $(H^+)$ . At the end of the second stage, the solution should correspond to one of disodium phosphate,  $Na_2HPO_4$ , in water. In a solution of this salt, the further ionization of  $HPO_4^{--}$  into  $H^+$  and  $PO_4^{---}$  is determined by the constant  $4 \times 10^{-13}$ , and its hydrolysis by the constant  $1 \times 10^{-14} \div 2 \times 10^{-7}$ . The net effect is a relatively large increase in  $(OH^-)$ . Actual measurements of the value of  $(H^+)$  during the titration of a 0.1 molal solution by means of the hydrogen electrode show inflections corresponding to the first and second stages of the titration, which are symmetrical with respect to the points at which  $(H^+)$  has the value  $1 \times 10^{-5}$  and  $1 \times 10^{-10}$  respectively. These points can be recognized by use of methyl orange and phenolphthalein respectively, but the inflection of the curve at both of these points is

small and therefore the end points are but poorly defined. It is possible, then, to titrate orthophosphoric acid by using methyl orange and assuming that it is monobasic, or by using phenolphthalein and assuming that it is dibasic.

If both the dissociation constants of a dibasic acid are large, the different stages in the process of neutralization are not easily recognizable. In the titration of sulfuric acid for example, the titration curve shows no appreciable inflection where the first stage has been completed but a very decided inflection at the completion of the second.

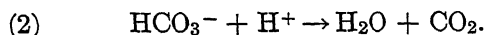
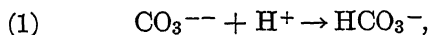
**Titration of Bases.** The theory of the titration of bases is analogous to that of the titration of acids. Strong bases, which include all the alkaline hydroxides, can be satisfactorily titrated with a strong acid by use of any of the indicators listed. In titrating weak bases, indicators found at the upper end of the series, whose sensitiveness toward  $H^+$  is but slight, should be used. Many of the organic bases are too weak to be titrated successfully.

The possibility of directly titrating the slightly soluble inorganic bases and oxides depends upon their solubility as well as their dissociation constants, most of which are unknown. The determining factor is the value of  $(H^+)$  in a saturated solution of the base. In solutions of calcium hydroxide, this is so small that direct titration is possible. Such substances as zinc oxide have almost no effect on  $(H^+)$  and can only be determined by back titration, that is by using an excess of standard acid and determining the excess added with a standard base.

✓ **Titration of Salts of Weak Acids with a Strong Acid.** The data represented by the graphs of Fig. 55 indicate that it should be possible to titrate certain salts which yield a strong cation and a very weak anion with a strong acid if an indicator which is only slightly sensitive to  $H^+$  is used. Actual experience shows that accurate results can be obtained if the anion is so weak that the dissociation constant of the corresponding acid is not greater than  $1 \times 10^{-8}$ . This is clearly indicated by the graphs referred to. For salts which yield stronger anions, it becomes necessary either to titrate with a chosen indicator to a specific color shade or to make use of the hydrogen electrode. If the weak anion is di- or tri-valent, the titration curve may show two, or even three,

inflections. The preceding statements relating to the titration of phosphoric acid show that it should be possible to titrate such substances as sodium orthophosphate with a strong acid, using either phenolphthalein and assuming that the equivalency is one, or methyl orange and assuming that the equivalency is two. This suggestion is confirmed by actual experience.

In the titration of sodium carbonate there are two stages recognizable, corresponding to the equations:



During the first stage ( $\text{H}^+$ ) is determined almost entirely by the hydrolysis of  $\text{CO}_3^{--}$ , which is determined by the constant  $1.67 \times 10^{-4}$ . This is obtained by dividing the dissociation constant of water by that representing the second stage in the dissociation of carbonic acid, which reduces ( $\text{H}^+$ ) at the end point to a value which can be recognized by phenolphthalein. During the second stage ( $\text{H}^+$ ) is determined by the net result of the tendency of  $\text{HCO}_3^-$  to undergo further ionization on the one hand and hydrolysis on the other. The former is determined by the constant representing the first stage in the dissociation of carbonic acid, which is  $3 \times 10^{-7}$ , and the latter by  $1 \times 10^{-14} \div 3 \times 10^{-7}$  or  $3.3 \times 10^{-8}$ . There must also be considered the decomposition of  $\text{HCO}_3^-$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and the limited solubility of the former. As soon as saturation with  $\text{CO}_2$  is attained, ( $\text{H}^+$ ) should remain practically constant during the rest of the titration. Experience shows that this value is less than that required to give the acid color of methyl orange, and, therefore, the point at which the strong acid used for the titration is in excess can be recognized with this indicator.

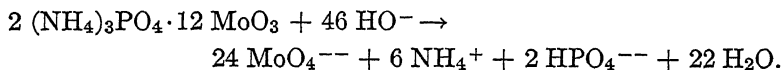
**Titration of Salts of Weak Bases with Strong Bases.** The theory of the titration of salts which yield a strong anion and a weak cation is analogous to that of the process discussed in the preceding section. Such titrations are not possible unless an indicator can be found which is not affected by the  $\text{HO}^-$  of the liberated base, but is affected by very small concentrations of the base of the titrating solution used. Those indicators which



are very sensitive toward  $H^+$  are therefore the ones to be used in these titrations.

**Titration Which Involves a Previous Separation.** A large number of substances which cannot be determined directly by titrating with an acid or base may be transformed into substances which can be so determined. This includes a large number of the metallic elements which form insoluble salts with weak acids. Thus, although calcium when present as a salt cannot be titrated directly, it can be precipitated from its solutions as a carbonate, filtered and washed, and then titrated like any other salt which represents a combination of a weak acid and a strong base. The accuracy of the process depends upon the insolubility of the precipitate, upon the completeness with which the precipitating agent, in this case ammonium carbonate, can be washed out, and upon the accuracy of the final titration.

Another illustration is found in a method which is largely used for the determination of phosphoric acid when in the form of its salts. It is based upon the fact that this acid is, under proper conditions, completely precipitated by ammonium molybdate as ammonium phospho-molybdate,  $(NH_4)_3PO_4 \cdot 12 MoO_3$ , which reacts with a solution of sodium hydroxide as follows:



As this reaction is practically complete and instantaneous, we can titrate the  $MoO_3$  combined with the ammonium phosphate, and the amount of phosphorus present can be calculated from the assumption that every 12 molecules of  $MoO_3$  found represent 1 molecule of phosphoric acid originally present.

**Titration Which Involves the Use of a Special Reagent to Increase Dissociation.** In a limited number of instances, the desired transformation can be effected by the use of a reagent which does not itself react with the titrating solution, and in such determinations previous separation of the product is not necessary. Thus, hydrocyanic acid, whose acidic properties are too weak to admit of a direct titration, can be completely changed into mercuric cyanide and hydrochloric acid by the addition of mer-

curic chloride, and the resulting hydrochloric acid can be titrated with accuracy. The process owes its accuracy to the remarkably low dissociation constant of mercuric cyanide.

### Questions and Problems. Series 24

1. Calculate ( $H^+$ ) at the true end point when 40 cc. of a 0.1 N solution of an acid ( $k = 1 \times 10^{-6}$ ) is titrated with a 0.2 N solution of a base ( $k = 1 \times 10^{-6}$ ). Would you expect a large inflection of the titration curve at the true end point?

2. Calculate ( $H^+$ ) in a mixture composed of 50 cc. of 0.1 N acid ( $k = 1 \times 10^{-6}$ ) and 22 cc. of a 0.2 N base ( $k = 1$ ). *Ans.*  $1.35 \times 10^{-7}$ .

3. Calculate ( $H^+$ ) in a mixture composed of 25 cc. of 0.1 N sodium cyanide ( $K$  for HCN  $= 7 \times 10^{-10}$ ) and 26 of 0.1 N hydrochloric acid, assuming the final volume is 100 cc. and no HCN is volatilized. *Ans.*  $1 \times 10^{-3}$ .

4. Calculate ( $H^+$ ) at the true end point in titrating 40 cc. of a 0.1 N solution of sodium benzoate (for benzoic acid,  $K = 6.86 \times 10^{-5}$ ) with a 0.2 N solution of hydrochloric acid assuming the final volume is 100 cc. *Ans.*  $1.66 \times 10^{-3}$ .

5. Suggest a buffer mixture which would maintain the value of ( $H^+$ ) at  $1 \times 10^{-3}$ .

6. What experimental procedure would you use in order to prepare a solution whose composition is the same as that at the true end point in the titration of sodium lactate with hydrochloric acid?

7. The acid color of a certain indicator is red, and its basic color is yellow. In a solution in which ( $H^+$ ) is  $1 \times 10^{-7}$ , it yields a particular shade of orange which is identical with that of a solution containing the same concentration of indicator, in which the indicator is known to be one-half transformed; what is the value of the indicator constant? *Ans.*  $1 \times 10^{-7}$ .

8. Show why it should or should not be possible to determine by titration with a strong acid; sodium borate,  $NaBO_2$ ; potassium salicylate,  $C_7H_5KO_3$ , or potassium succinate,  $C_4H_4K_2O_4$ .

9. Show why it should or should not be possible to titrate with a strong base; potassium bitartrate,  $C_4H_5KO_6$ ; sodium bisulfite,  $NaHSO_3$ ; or sodium tetroxalate,  $H_2C_2O_4 \cdot NaHC_2O_4 \cdot 2H_2O$ .

10. Suggest possible direct or indirect methods for the determination, by titration with an acid or a base, of (a)  $ZnSO_4$ , (b)  $Al_2(SO_4)_3$ , (c)  $CaO$ , (d) HCN.

## CHAPTER XXXII

### **DETERMINATIONS WITH STANDARD SOLUTIONS OF AN ACID AND A BASE**

#### **I. Preparation of a Standard Acid and a Standard Base**

**Choice of the Acid and Base.** As noted on page 307 it is essential that the acids and bases used for the preparation of standard solutions have large dissociation constants. It is also desirable that they shall be stable compounds, that their action on the glass vessels used to retain them be small, and that they exercise no oxidizing or reducing action on the indicators used. These considerations limit the acids generally used to hydrochloric and sulfuric. For bases the hydroxides of sodium and potassium are most frequently employed, but the hydroxides of ammonium and barium are sometimes to be preferred.

Every titration should require the use of a moderately large volume of the standard solution; hence in titrating substances of low percentage composition either a large amount of sample must be used or the concentration of the solution used must be small. On the other hand, strong solutions give more decisive end points than weak ones and their strength is changed to a less extent relatively by carbon dioxide which is gradually absorbed from the atmosphere, especially by basic solutions. In general it is not desirable to use solutions of acids or bases stronger than one-half, or weaker than one-tenth normal, although special circumstances may make it desirable to vary these limits.

The preparation of half-normal solutions of sodium hydroxide and hydrochloric acid will be described here. In preparing these solutions it is desirable to eliminate the carbonate, which is always present in even the purest obtainable caustic soda, and also the carbon dioxide in the distilled water used.

**Procedure for Preparation of Solutions.** Weigh out on a rough

balance 50 grams of pure sodium hydroxide, place in a 2500-cc. flask, add 2 liters of distilled water and shake occasionally until the alkali is completely dissolved. Next add about 5 grams of finely powdered C. P. calcium oxide and allow the mixture to stand

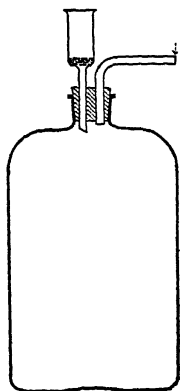


Fig. 57.— Device for filtering alkali solution

for an hour with occasional shaking, or still better allow it to stand over night. Place a Witt filter-plate in a filtering tube and provide with a good thickness of washed asbestos in the customary manner; connect the filter tube with a clean two-liter bottle as shown in Fig. 57 and filter the alkali solution into the bottle. Keep the bottle stoppered as far as possible.

Measure out 100 cc. of concentrated C. P. hydrochloric acid into a clean two-liter bottle, dilute to 2 liters with water which is free from carbon dioxide and mix thoroughly. To determine whether the carbon dioxide is present in objectionable amounts add one drop of phenolphthalein indicator to 200 cc. of the water in question, and then one drop of the approximately semi-normal alkali solution; if the mixture does

not acquire a distinct pink color the amount of carbon dioxide is excessive, and the water must be heated to the boiling point to remove it.

**Procedure for the Standardization.** Ignite and weigh accurately an 8-cc. platinum crucible, add about 1 gram of pure sodium carbonate weighed roughly, and heat cautiously until the carbonate barely fuses, then allow to cool and weigh accurately. Place the crucible in a 200-cc. beaker, add 50 cc. of water and 1 drop of methyl orange indicator. Place a piece of white paper under the vessel and then add the acid solution from a burette until the mixture finally becomes permanently of a salmon red color. If the proper stage in the titration has been reached an additional drop of the acid will produce a clear light red color. Make a second determination as a check. The two results should not differ by more than one part in 500.

Divide the weight of carbonate used by the volume of acid used for the titration, then divide this quotient by the weight of sodium

carbonate which should be present in 1 cc. of a normal solution of sodium carbonate. This gives the normality of the acid solution.

Measure out 25 cc. of the base solution, dilute with 50 cc. of water, add methyl orange indicator and titrate exactly as in the titration of the sodium carbonate. Repeat the titration until the relation between the strength of the acid and base has been determined to within one part in 500. Calculate from this relation and from the normality of the acid solution the normality of the base solution.

**Reduction to Semi-normal Strength.** Calculate the volumes to which 1500 cc., or some other convenient volume, of both acid and base solutions should be diluted in order to make both solutions exactly semi-normal strength, and add the calculated amount of water, assuming that neither contraction nor expansion takes place. In making this dilution first rinse out a 1000-cc. and a 500-cc. flask with a little of the solution and discard; then fill the flasks to the mark with the solution and discard whatever remains in the bottle, but do not rinse the latter with water; next drain the contents of the two flasks into the bottle and add the calculated amount of water which should be measured accurately from a burette.

Re-determine the volumetric ratio between the two solutions. If it differs from one by more than two parts in one thousand faulty work has been done and, since the error may be in either one or both of the two solutions, the standardization with pure sodium carbonate must then be repeated. If difficulty is experienced in attaining the requisite accuracy by this method standardize the acid solution by the gravimetric method described below. If either of the solutions has been diluted to below semi-normal strength it is not necessary to prepare a new solution, but the exact factor representing the relation of the solution to normal strength should be calculated and used in place of the factor one-half wherever this factor would have been used.

**Gravimetric Method of Standardization.** Remove with a pipette 25 cc. of the acid solution, dilute to 200 cc. and add a slight excess, that is about 10 per cent more silver nitrate than is theoretically required to react with the chlorine present. Heat the mixture to boiling and stir until the precipitate coagulates, then

filter on an asbestos filter, wash, dry and weigh resulting silver chloride. Calculate the relation of the acid solution to normal strength from the weight of silver chloride obtained from each cubic centimeter of acid measured out. Calculate the relation of the alkali solution to normal strength from the volumetric ratio and the normal value of the acid solution.

## II. Experiments with Indicators

**Color Changes and Sensitiveness.** Prepare 100-cc. portions of 0.01 N hydrochloric acid and sodium hydroxide by dilution of some of the standard solutions already prepared. (a) Add 10-cc. portions of distilled water to 3 test tubes, *A*, *B* and *C*, and then 2 drops of phenol red indicator to each tube. To *A* add 1 drop of 0.01 N sodium hydroxide and to *C* the same amount of hydrochloric acid, and note the colors of the three solutions. Add successively additional drops of sodium hydroxide to *A* and of hydrochloric acid to *C* and note changes after each addition. What is the character of the color change and does the change occur when  $(H^+)$  is greater or less than  $1 \times 10^{-7}$ ? Is the difference large? (b) Perform a similar series of experiments substituting 1 drop of methyl orange and (c) 4 drops of phenolphthalein for methyl red. Arrange the three indicators in a table showing decreasing sensitiveness towards  $(H^+)$ .

**Action of Buffer Solutions.** (a) Add 10-cc. portions of 0.01 N sodium chloride to 3 test tubes, *A*, *B* and *C*, and then 2 drops of phenol red indicator to each. To *A* add 0.01 N sodium hydroxide and to *C* 0.01 N hydrochloric acid and compare results with the preceding corresponding experiments. (b) Add 10-cc. portions of ammonium acetate to 3 test tubes, *A*, *B* and *C*, and 2 drops of phenol red indicator to each tube. Add sodium hydroxide to *A* and hydrochloric acid to *C* as in the preceding experiments and compare results. How can you explain these differences? Would these differences be decreased or increased if you substituted ammonium hydroxide for sodium hydroxide and acetic acid for hydrochloric acid?

### III. Procedure for the Determination of Acidic Substances

**Determination of the Strength of Concentrated Sulfuric Acid.** Weigh accurately a clean glass-stoppered weighing bottle of about 10-cc. capacity. Prepare a clean and dry dropping-tube or pipette of about 3-cc. capacity, insert into the bottle containing the sample and fill about half full. Remove from the bottle and allow about 15 drops to flow into the weighing bottle; being careful to avoid spattering, then close the bottle and weigh accurately. Fill the bottle nearly full of water, mix and pour into a 200-cc. beaker, then rinse out at least three times with 10-cc. portions of water. Add a drop of the proper indicator and titrate with the standard alkali solution. Calculate the percentage of sulfuric acid by the use of the general formula.

**Determination of the Acidity of Vinegar.** The acidity of vinegar, unless adulterated with sulfuric acid, is due almost entirely to acetic acid. When titrated with a base the coloring matter present undergoes a gradual color change which is difficult to characterize. This change can be distinguished with fair accuracy from the color change of phenolphthalein if a large amount of the indicator is added and the solution diluted sufficiently. In extreme cases, that is, where the color is very intense, it may be necessary to remove it by the addition of bone-black and filtering, but since this reagent absorbs small quantities of acid its use should be avoided if possible. It is customary to report results in terms of the total weight of acid, calculated as acetic, per cubic centimeter of sample.

Measure out 10 cc. of the vinegar into a 400-cc. beaker and dilute with 200 cc. of water free from carbon dioxide. Add 3 drops of phenolphthalein and titrate with the alkali solution, disregarding the changes from brown to drab and endeavoring to recognize the point at which the pink of the phenolphthalein, modified to some extent by the drab color of the vinegar, becomes apparent. Calculate the weight of acetic acid in 1 cc. of sample.

**Determination of Potassium Bitartrate in Argol or Commercial Cream of Tartar.** The chief source of cream of tartar and tartaric acid is the argol which separates on the sides of the casks during the manufacture of wine. It contains in addition to potassium

bitartrate ( $\text{C}_4\text{H}_5\text{KO}_6$ ) salts of a number of organic acids and large amounts of coloring matter. The dissociation constant of the first hydrogen atom of tartaric acid is  $9.7 \times 10^{-4}$ , that of the second has not been accurately determined but it is sufficiently large to justify regarding it as a dibasic acid when titrated with a base if phenolphthalein is used as the indicator and therefore potassium bitartrate is one of the acid salts which can be titrated directly.

The large amount of coloring matter present in argol often make it difficult to recognize the true end point; the conditions observed in the titration of vinegar also apply here.

Weigh out 2 grams of the finely powdered sample, add 150 cc. of hot water and stir for a few minutes. If a large amount of insoluble matter remains, filter on a small filter and wash with hot water until the washings are free from acidity. Add 3 drops of phenolphthalein and titrate with the standard alkali solution. Calculate the percentage of potassium bitartrate.

**Determination of Anhydride in Natural Borates.** The naturally occurring borates, which include the minerals colemanite, ulexite and pandermite, are simple or double borates of calcium and sodium. They are usually associated with the carbonates and sulfates of the alkali metals and with clay and sand. As they are the source of most of the borax and boric acid of commerce the value of ores containing them depends upon the percentage of boric anhydride which they contain.

The dissociation constant of boric acid is so small that it is completely displaced from solutions of its salts by an equivalent amount of a strong acid; if the salts are insoluble an excess of the acid must be used. Even concentrated solutions of boric acid do not affect the color of methyl orange and hence this indicator can be used to determine the point at which all of the mineral acid but none of the boric acid in a mixture which contains both has been neutralized. Hence if a sample which contains any of the borates named is treated with an excess of hydrochloric acid and the mixture made to give a neutral reaction with methyl orange it will contain an amount of free boric acid which corresponds to the boric anhydride present. The free acid cannot be titrated directly even where phenolphthalein is used, but the addition of glycerine



or mannitol increases its acidic properties to such an extent that this titration then becomes possible. If glycerine is used it must form about 30 per cent by volume of the entire mixture; if mannitol is used 2 per cent by weight is sufficient, and the end point is more sharply defined.

The method is not affected by the presence of carbonates if the carbon dioxide which is liberated during the decomposition of the sample is expelled, but since boric acid is very slightly volatile long boiling must be avoided. The accuracy of the method depends largely upon the maintenance of the proper concentration of the reagents used.

Weigh out 1.5 grams of the finely ground sample into a 200-cc. beaker, add 5 cc. of dilute hydrochloric acid, warm gently and stir with a glass rod until the sample seems to be completely decomposed, then add 10 cc. of water and heat to 80° C. If a large amount of flocculent residue remains, filter on a very small filter but keep the volume of filtrate and washings to about 50 cc. Add a drop of methyl orange and then standard sodium hydroxide until the mixture has a clear lemon yellow color. Next add 3 drops of phenolphthalein and about 1 gram of mannitol and finally titrate with the standard alkali to a permanent pink color. Add another half gram of mannitol and if the color fades continue adding alkali until it is restored. As equilibrium is attained but slowly, more time should be allowed for this titration than for those previously described. Calculate the percentage of boric oxide assuming that each molecule has a neutralizing power of two.

#### IV. The Analysis of Commercial Alkalies

**Preliminary Statements.** The alkalies of commerce consist mainly of the hydroxides, carbonates and bicarbonates of sodium and potassium. Their total alkalinity can be accurately determined by a direct titration with a standard acid, using methyl orange as indicator; or, by using the process of back titration and heating the solution to drive off carbon dioxide, other indicators may be used. It is sometimes necessary to distinguish between the alkalinity due to hydroxides and carbonates and that due to carbonates and bicarbonates.

**Methods for the Determination of Hydroxides and Carbonates.**

If a solution which contains both hydroxides and carbonates is titrated with a standard acid, using phenolphthalein, the color change takes place when the hydroxide has been completely neutralized and the carbonate changed into bicarbonate; hence the difference between the result obtained for total alkalinity and that obtained by this method represents the acid needed to neutralize the bicarbonate formed from the normal carbonate originally present and it is possible to calculate both the hydroxide and carbonate originally present. As the end point in the latter titration is very unsatisfactory, this method is used only for approximate determinations.

A more satisfactory method of making this determination depends upon the addition of sufficient barium chloride to precipitate all of the carbonate and titration of the hydroxide in the resulting mixture. If the concentration of hydrogen ion which is attained in making this titration is not too large it is not necessary to remove the precipitated calcium carbonate. It is preferable, therefore, to use an indicator which is affected by a small concentration of hydrogen ion.

**Outline of Method for the Determination of the Hydroxide and Carbonate of Soda in Commercial Caustic Soda.** Weigh accurately a glass weighing bottle of about 10-cc. capacity and transfer to it as rapidly as possible about 10 grams of the roughly powdered and mixed sample, and again weigh accurately. Empty into a small beaker, add about 50 cc. of carbon-dioxide-free water and stir until the sample is dissolved. Pour into a 250-cc. graduated flask and rinse out both bottle and beaker with more water, cool to the normal temperature, dilute to exactly 250 cc. and mix thoroughly. The very small amount of insoluble residue sometimes found may be allowed to settle and is disregarded.

Measure out 25 cc. of the solution, add 50 cc. of water, a drop of methyl orange and titrate with the standard acid. Remove a second 25-cc. portion, add 50 cc. of water, 5 cc. of reagent barium chloride, a drop of phenolphthalein and titrate with the standard acid, adding the latter very slowly as the titration approaches completion. Calculate the percentages of sodium hydroxide and sodium carbonate present.

### ✓ V. Determination of Crude Protein in Flour

**Theory of the Method.** The proteins represent a group of extremely complex nitrogen-containing compounds, which form one of the three classes of nutrient materials present in foods. Although the percentage of nitrogen present varies somewhat, experience has shown that protein can be determined with fair accuracy by multiplying the percentage of nitrogen present by a factor which varies somewhat with the nature of the proteid concerned. For the protein in flour the factor commonly used is 5.7, for that of meat 6.38 is used. The results obtained by this method are always designated as "crude protein."

When flour is heated with concentrated sulfuric acid the acid is gradually reduced to sulfur dioxide and water, while the carbon and hydrogen of the flour are oxidized to carbon dioxide and water and the nitrogen is changed to ammonium sulfate. When the resulting solution is distilled with an excess of a strong base ammonia is formed and distills over and can then be determined by titrating with a standard acid. Under certain conditions these operations can be carried out quantitatively, and form the basis of the Kjeldahl method which, with its various modifications, is used for the determination of all classes of nitrogen-containing compounds.

**The Apparatus Needed.** The Kjeldahl method involves two groups of operations. The digestion must be made in a round-bottomed flask, which is not easily broken by the large changes in temperature to which the different parts of it are subjected; flasks made of Jena or "pyrex" glass are commonly used. Since large amounts of sulfur dioxide and sulfur trioxide are formed this operation should be carried out in a hood which has a good draft, or each flask must be connected directly with a suction apparatus. The "distillation" must be made in a still, which is provided with a special form of still-head designed to prevent any of the boiling liquid from being carried over into the receiver while the distillation is in progress. Since the time needed for both of these operations may be long, most laboratories are provided with special multiple-unit pieces of apparatus, in which the digestion and distillation of from 3 to 20 samples can be made

simultaneously. In such an apparatus, which is represented in Fig. 58, the condenser consists of a narrow trough of sheet copper through which water slowly circulates; the condenser tubes are made of block tin, as this metal is not affected by dilute ammonium hydroxide.

**Outline of Method of Procedure.** Weigh out about 2 grams of the sample into a 500-cc. Kjeldahl flask, which should be made

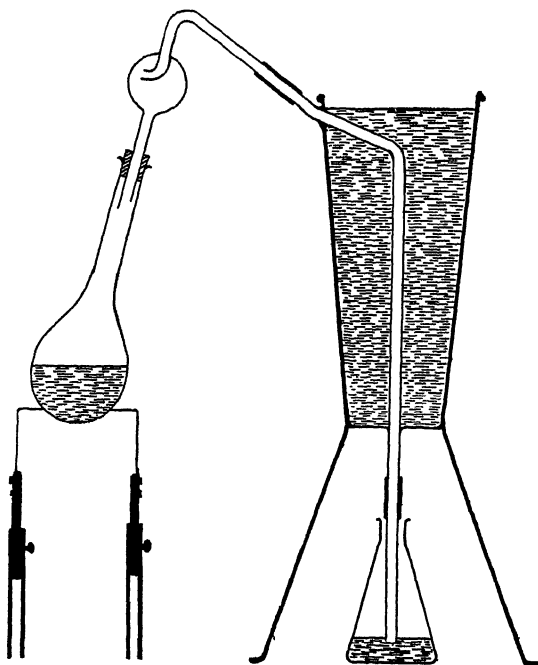


Fig. 58.—Illustrating Kjeldahl apparatus for determination of nitrogen.

of hard glass. Add 20 cc. of concentrated sulfuric acid, using it to rinse down any particles of the sample which adhere to the sides of the flask, and then add about 0.7 gram of mercuric oxide for the purpose of increasing the speed of the reaction. Place the flask in an inclined position on a cold sand bath and heat gently for ten minutes or until violent frothing ceases, then raise the temperature to the boiling point and boil vigorously until a color-

less solution is obtained. Remove from the rack, allow to cool slightly, and add a few grains of solid potassium permanganate, using sufficient to produce a slight but permanent pink or green color. Allow to cool, dilute to 200 cc. and again cool under the tap to the temperature of the room.

Add to the receiver of a distilling apparatus 10 cc. of semi-normal hydrochloric acid, 50 cc. of water and 1 drop of methyl orange. Place the delivery tube attached to the distillation apparatus inside the receiver and adjust the level of the latter until the end of the delivery tube touches the surface of the liquid in the receiver.

Add to the solution in the Kjeldahl flask 50 cc. of a 50 per cent solution of sodium hydroxide, then 10 cc. of a 5 per cent solution of potassium sulfide (to precipitate the mercury) and 2 grams of granulated zinc (to prevent boiling over) and at once connect with the still-head by means of a good rubber stopper.

Heat to boiling and continue distilling until the volume of the solution in the receiver amounts to 200 cc. Remove the receiver, rinse out the delivery tube and titrate with a one-tenth normal solution of ammonium hydroxide. Calculate and report the percentage of crude protein present.

## VI. Questions and Problems. Series 25

1. If the water used in preparing the standard acid had been saturated with carbon dioxide, how and under what conditions would it have affected the results obtained with this solution?

2. If the sodium carbonate used had contained 1 per cent of potassium carbonate, how would the results obtained with the standard acid and standard base have been affected?

3. A solution of sulfuric acid is prepared by weighing out 5 grams of pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , dissolving in water, and precipitating the copper by electrolysis; if this solution is diluted to 1000 cc., what relation does it bear to normal?

4. Calculate by the simplest method the normality of solutions of sodium hydroxide 1 cc. of which react with (a) 0.02 gram of benzoic acid,  $\text{C}_6\text{H}_5(\text{COOH})$ ; (b) 0.04 gram of succinic acid,  $(\text{CH}_2)_2(\text{COOH})_2$ ; 0.015 gram of crystallized oxalic acid,  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

5. Calculate by the general formula the percentage of citric acid, a tri-basic acid of the formula  $\text{C}_6\text{H}_8\text{O}_7$ , if the weight of mixture used was 0.643 gram, the volume of KOH solution used for the titration was 31 cc. and 1 cc. of KOH solution = 0.015 gram of pure oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ).

## 342 FUNDAMENTALS OF QUANTITATIVE ANALYSIS

6. Calculate the percentage of  $P_2O_5$  in a solution of  $H_3PO_4$  if the weight of solution used was 6.43 grams, volume of KOH solution used for the titration (with methyl orange) was 26 cc., and 1 cc. of KOH solution contained 0.016 gram.

7. Show how  $B_2O_3$  could be determined in pure borax more easily than in calcium borate.

8. Explain why the  $BaCO_3$  precipitated in the analysis of caustic soda has no effect on the titration. Is there any objection to using methyl orange for the titration? Is there any objection to filtering off and washing the  $BaCO_3$  precipitate?

9. Calculate by the simplest method the volume of semi-normal acid required to neutralize the ammonium hydroxide produced by distilling 1 gram of  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$  with an excess of KOH.

10. How would you prepare a solution of HCl so that each cubic centimeter should equal exactly 0.01 gram of  $NaNO_3$ , when the latter was determined by reducing to an ammonium salt, distilling with an excess of KOH and titrating the distillate with the HCl solution?

## SECTION IX

### VOLUMETRIC PROCESSES INVOLVING OXIDATION

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#### CHAPTER XXXIII

##### ✓GENERAL FEATURES OF VOLUMETRIC PROCESSES INVOLVING OXIDATION AND REDUCTION

**Definition of Oxidation and Reduction.** Certain quantitative processes, which involve oxidation and reduction, were considered in Chapter XIII in describing the use of an electric current as a means of precipitating certain substances. Many reactions involving oxidation and reduction, in which all the substances concerned are soluble, as well as some in which insoluble compounds are concerned, are used as the basis of important volumetric processes, and a more elaborate discussion of the factors affecting the completeness of all reactions belonging to this category becomes necessary.

The term oxidation is here used in its broadest sense and includes all changes involving a loss in the number of electrons associated with a given atom or group of atoms. Reduction represents the converse of this and the two reactions are necessarily reciprocal, that is, when one substance is oxidized some other substance must be reduced, and the total amount of oxidation effected must equal the total amount of reduction effected. If the distinction between positive and negative valence be recognized such reactions are always associated with a change in valence. According to this conception the valence of any uncombined element is always zero and that of the element in a compound corresponds to the number of positive or negative valences exercised by one atom of the element concerned. In estimating the valence of an

element it is usually assumed that the valence of combined hydrogen is plus one although there are some compounds, such as the hydrides of certain metals, in which hydrogen must have a negative valence. It is also assumed that the valence of combined oxygen is minus two and of combined fluorine is minus one. By using these three elements as standards of comparison it is usually possible to fix the valence of any element in a compound with a fair degree of assurance. Thus, the valence of arsenic is minus three in arsine and plus three in arsenious oxide, and the valence of uranium in uranyl ion ( $\text{UO}_2^{++}$ ) is plus six.

**Equivalency of Oxidizing and Reducing Agents.** Since oxidation is measured by the increase and reduction by the decrease in valence, and since the total amount of oxidation must equal the total amount of reduction, the number representing the sum of all the increases in valence must equal the number representing the sum of all the decreases in valence in any balanced equation representing such reactions. Further, since the change in the valence of the hydrogen atom, resulting from its oxidation, is the unit with which the changes in valence of all oxidizing and reducing agents are compared, the equivalent values of such reagents must equal the atomic or molecular weights divided by the number representing the sum of all the valence changes which the elements composing the substance in question undergoes. This number is therefore the "equivalency" of the substance concerned, provided it is used in a reaction in which it undergoes this particular oxidation or reduction. In many cases only one atom of the molecule experiences a valence change. Thus when a stannous salt is oxidized to a stannic salt the only atom oxidized is tin and since its valence changes from plus two to plus four the equivalency of the entire molecule is two. When potassium dichromate is used as an oxidizing agent both of the two chromium atoms are reduced from plus six to plus three; the total valence change and therefore the equivalency of the entire molecule is six. The equivalency of an oxidizing agent may also be defined as the total number of positive valences furnished to, or of negative valences taken from, the substance oxidized by one molecule of the agent. The equivalency of a reducing agent may be defined by the converse statement.



**Oxidation and Ionization Changes.** Many oxidizing and reducing agents are strong electrolytes and the actual changes which they undergo are changes in the nature of the ions formed. Frequently the changes involve nothing more than the addition or removal of electrons. If electrons are removed the process is clearly oxidation; if electrons are added the process is clearly reduction. Thus the oxidation of a stannous salt in solution is actually represented by a decrease of two in the number of electrons associated with the tin atom. The reduction of permanganates to manganates in solution is actually represented by an increase in the negative charge of the  $\text{MnO}_4$  radical from one to two. In other cases the change is more complex and involves addition to or removal of atoms from the ion concerned, and neither the valence of the element nor the change in valence can be estimated from the changes in the associated charges only. Thus in estimating the valence of chromium in dichromate ion it is necessary to take into consideration both the number of oxygen atoms and the number of negative charges associated with the ion. The seven oxygen atoms have a valence of minus fourteen but two of these represent the charge of minus two on the ion; hence, the two chromium atoms must have a value of plus twelve, or plus six for each atom. In representing reactions of this kind by means of equations it is desirable always to represent so far as is possible the actual changes which take place and avoid the use of either ions or unionized substances the existence of which is purely hypothetical. Thus it is sometimes incorrectly assumed that the dichromate solution contains ions consisting of a single atom of chromium associated with six positive charges.

**Equilibrium in Oxidizing Reactions.** Theoretically all reactions between equivalent amounts of oxidizing and reducing agents are more or less incomplete provided the reaction is one to which the principle of chemical equilibrium applies, that is, provided it is a reversible process. The completeness of such reactions and therefore the value of the equilibrium constant depends upon the sum of the intensities or the chemical potentials of the oxidizing and reducing processes concerned. The relative magnitude of these potentials can be ascertained by comparing the ability of different oxidizing agents to oxidize a series of reducing agents or vice versa.

By such a procedure it is possible to arrange all such reagents in a series which indicates the relative oxidizing intensities of each of the reagents given. In such a table the most powerful oxidizing agent would appear at the top and the most powerful reducing agent at the bottom of the list. Furthermore, the most complete oxidizing-reducing reaction possible would be the one between the reagent at the top and the one at the bottom of the list.

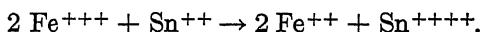
Direct measurements of the equilibrium constants of such reactions are difficult to make owing to the difficulty of determining the very small concentrations of the reagents left uncombined and very few measurements of this kind have been made. As already noted in Chapter XIII the electromotive force available when reactions involving oxidation and reduction are made to take place in such a manner as to generate electrical energy, furnishes an accurate method of estimating the completeness of such reactions.

**Chemical Potentials between Ions.** The table of electrode potentials on page 160 includes many reactions in which none of the reagents is a conductor of the first-class. Such reactions cannot be used as components of a galvanic cell unless some metallic conductor is present which can take up the electrons made available by the reaction in question and deliver them to the external circuit, or carry electrons taken from the external circuit to points in the solution at which they can be used by the reaction in question. The metallic conductors used for electrodes must not be chemically acted upon by the substances in solution, that is, must give zero potential with the various components of the solution. For solutions of most oxidizing agents, except the halogens, plates of platinum or iridium are used, and it is believed that the potential difference established on them is a true measure of the electrode potentials of the reactions concerned.

It should be noted that in all such reactions the concentrations, or more accurately the activities, of more than one of the reagents concerned are variable and the actual value of the electrode potential of any solution depends upon more than one concentration. If only two reagents are concerned the value of the electrode potential depends upon the ratio between these concentrations, and not upon their absolute values. The figures given for normal

potentials assume that all concentrations, except those of insoluble reagents, are molal; but for reactions in which all reagents are soluble, the values given are equally correct for any solution in which the ratio of the two concentrations is one. When three or more reagents are concerned the relation is more complex.

**Use of the Table of Electrode Potentials.** In order to show how the completeness of the reactions under discussion can be calculated we will consider the reaction



The two electrode reactions are (1)  $\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$  and (2)  $\text{Sn}^{++} \rightarrow \text{Sn}^{++++} + 2e$ . The table on page 160 gives + 0.74 volt for (1), if assumed to take place in the direction here given, and - 0.13 for (2). The net voltage available, provided all four ions are of equal concentration is, + 0.61, which is large enough to indicate a fairly complete reaction. If it is assumed that we start with a mixture containing equivalent amounts of ferric and stannous ion the solution must at all times contain equivalent amounts of ferrous and stannic ion and also of ferric and stannous ion. Further, if it is assumed that the progress of the reaction can be stopped at any desired point the actual values of both potentials can be calculated at any desired stage of completion. If it is assumed that the reaction is stopped when only one one-thousandth part of the iron is reduced and an equal fraction of the tin is oxidized the potentials are;

$$(1) \quad E = + 0.74 - 0.059 \log (1 \div 999) = + 0.9170,$$

$$(2) \quad E = - 0.13 - 0.0295 \log (1 \div 999) = - 0.0415.$$

Hence, the total voltage is + 0.8755. If it is assumed that the reaction is stopped when only one one-thousandth part of the iron is left unreduced and of the tin is left unoxidized the potentials are:

$$(1) \quad E = + 0.74 - 0.059 \log (999 \div 1) = + 0.5630,$$

$$(2) \quad E = - 0.13 - 0.0295 \log (999 \div 1) = - 0.2185.$$

Hence the total voltage of the cell is + 0.3445. As the reaction progresses the positive value of (1) decreases and the negative

value of (2) increases and the limit of both processes is attained when the sum of the two values is zero, which is the point at which equilibrium has been attained. If  $x$  represents the ratio of ferrous to ferric and also of stannic to stannous ion at this point we are justified in formulating the expression,

$$+ 0.74 - 0.059 \log x + (-0.13 - 0.0295 \log x) = 0,$$

from which  $0.0885 \log x = 0.61$  and  $x = 7.8 \times 10^6$ .

This shows that little more than one ten-millionth part of the iron is left unreduced, and of the tin is left unoxidized, when the two electrode potentials become  $+0.334$  and  $-0.334$  respectively. The changes in the values of the individual potentials have also been calculated for a number of assumed intermediate steps in the progress of the reaction and plotted as ordinates against percentage completion as abscissas in Fig. 59.

These graphs do not correctly represent the changes in potentials during an actual titration. In an actual titration one reagent is slowly added to the other and the one which is added is in the presence of an excess of the other until the true end point is reached. The equilibrium is readjusted after every addition, and it is still true that at every stage of the titration the positive potential of the oxidizing agent equals the negative potential of the reducing agent, but the ratios of the two concentrations which determine the values of each of these potentials are very different. If it is assumed that nine-tenths of an equivalent of stannous ion is added to a liter of solution containing one equivalent of ferric ion, the solution contains at the outset one mol of ferric and 0.45 mol of stannous ion. If we let  $x$  represent the fraction of ferric ion reduced at equilibrium we have the expression.

$$0.74 - .059 \log \frac{x}{1-x} + \left[ -0.13 - 0.0295 \log \left( \frac{0.5x}{0.45 - 0.5x} \right) \right] = 0.$$

Evidently the value of  $x$  approaches 0.9 as a limit, but if it reaches this limit the potential of the stannous-stannic couple becomes infinity. In order to satisfy the equation  $x$  must have a value which differs from 0.9 by about  $1 \times 10^{-18.8}$  and the fraction of ferric iron left unreduced is enormously large as compared with the

fraction of tin left unoxidized. This is a necessary consequence of the fact that ferric ion is in excess.

**More Complex Oxidation Reduction Reactions.** The factors affecting the completeness of reactions in which more than two concentrations are concerned will be studied by considering the use of permanganate ion as an oxidizing agent, although many

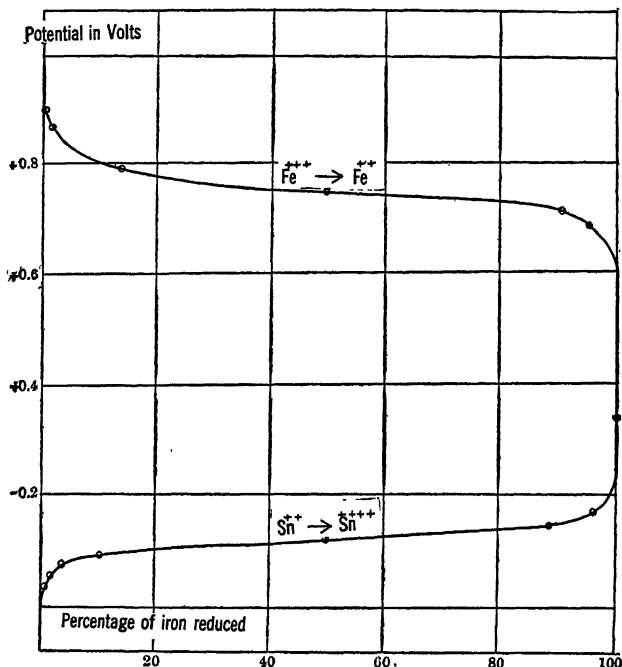
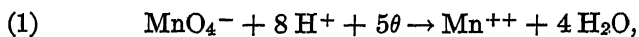


Fig. 59.

of the reactions in which permanganate ion is so used are not reversible processes. The reduction of permanganate to manganous ion is associated with the removal of oxygen from the permanganate ion through the formation of water with hydrogen ion. Since the manganese is changed from an acidic to a basic element hydrogen ion must be used up or the solution will become basic. The process is represented by

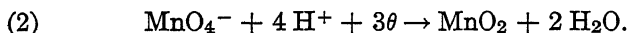


in which the equivalency of the permanganate ion is evidently five. The  $E_0$  value given in the table of electrode potentials is 1.48, which value assumes molal concentrations of permanganate, manganous and hydrogen ion. The potential for any solution can then be calculated from the expression

$$E = + 1.48 - \frac{0.059}{5} \log \frac{(\text{Mn}^{++})}{(\text{MnO}_4^-) \cdot (\text{H}^+)^8},$$

in which the concentration of water has been eliminated, as it is assumed that the solution is very dilute. It is evident that the value of  $E$  must be greatly affected by variation in  $(\text{H}^+)$ . If it is assumed that the ratio of manganous to permanganic ion remains constant, increasing the value of  $(\text{H}^+)$  by the factor ten must increase  $E$  by 0.0944 volt.

The table of electrode potentials gives another reaction, in which permanganate ion is reduced, corresponding to the expression



The  $E_0$  value given is 1.586 and since manganese dioxide is but slightly soluble and its concentration can vary but slightly the value of the potential for the process corresponds roughly to the expression

$$E = + 1.586 - \frac{0.059}{3} \log \frac{k}{(\text{MnO}_4^-) \cdot (\text{H}^+)^4}.$$

If  $\text{MnO}_4^-$  is kept constant the value of  $E$  will increase by 0.0787 volt for every increase in  $(\text{H}^+)$  by the factor ten.

The free energy changes of the two reactions, when all variable concentrations are molal, are

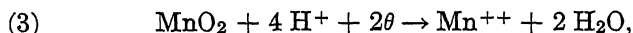
$$(1) \quad -\Delta F = \frac{5 \times 96500 \times 1.48}{4.185},$$

and

$$(2) \quad -\Delta F = \frac{3 \times 96500 \times 1.586}{4.185},$$

and therefore the tendency for (1) to take place exceeds that for (2) to take place. Obviously, however, decreasing  $(\text{H}^+)$  will

reduce the free energy of (1) more rapidly than that of (2) and there must be a certain value of  $(H^+)$  at which the two free energies become equal. Both reactions however are possible for a wide range of values of  $(H^+)$ , that is, give negative values for their free energy, and the relative values of the rates at which they proceed will determine which of the two actually take place in any given solution. It should also be noted the  $E_0$  value for (1) has never been successfully determined by a single direct measurement because it has not been possible to find conditions at which the reverse process proceeds with appreciable speed. The value given in the table has been calculated from the  $E_0$  value for (2) and that for a third reaction, namely



which has been found to be + 1.33 volts. The free energy of (1) must equal the sum of the free energies of (2) and (3) from which  $E_0$  for (1) can be calculated as follows:

$$\Delta F \text{ for (2)} = -96,500 \times 3 \times 1.586 = -96,500 \times 4.758,$$

$$\Delta F \text{ for (3)} = -96,500 \times 2 \times 1.33 = -96,500 \times 2.66$$

hence,

$$\Delta F \text{ for (1)} = -96,500 \times 5 \times 1.483 = -96,500 \times 7.418.$$

In the actual use of solutions of permanganate ion for the determination of substances which can be oxidized by it, the following additional items should be kept in mind. First, the oxidation of certain substances, such as nitrous acid, involves the formation of hydrogen ion, and therefore the effect of varying the concentration of the hydrogen ion in the solution for the whole process is less than that noted in the earlier part of this paragraph for the reduction of permanganate ion to manganous ion. Second, many of the reactions between permanganate ion and reducing agents are not reversible and the completeness of such reactions is determined by the speed at which they take place. Third, the simple equations which are usually employed to represent such reactions may give an incorrect idea of the mechanism of the process. This may involve a number of intermediate steps, all of which are associated with a decrease of free energy, but proceed at very different rates of speed.

This may result in a much less complete oxidation of the substance being determined than the free energy of the simple reaction demands.

**Recognition of End Points.** Many devices are made use of in recognizing the point at which an equivalent amount of the standard oxidizing or reducing agent has been added to the reducing or oxidizing agent being titrated. Those reactions which show pronounced color changes at or near the true end point require no indicator. Thus, the titration of oxalate by permanganate ion yields manganous ion and carbon dioxide, neither of which imparts a perceptible color to the mixture, whereas the permanganate ion does. A single drop of a tenth normal solution of this reagent is sufficient to give a perceptible color to 200 cc. of water and by titrating with it, the mixture shows a recognizable pink color at the apparent end point which is found to coincide very nearly with true end point. The color change in the titration of ferric ion with stannous ion is less satisfactory. Stannous and stannic ions are colorless; the color of ferrous ion is fairly intense at ordinary temperatures and is greatly intensified by heating to 80°. If the solution of ferric salt being titrated is kept hot and concentrated the true end point can be recognized by noting the point at which the yellow color changes to a light shade of green, with a fair degree of accuracy.

The addition of another reagent to act as an indicator makes it necessary to consider four additional equilibria since the added reagent may react with either of the two reagents used or with either of the two products formed by their interaction. Thus if we desire to find a good indicator for use in the titration of ferric ion with stannous ion we would require a reagent which would give either (a) a decided color reaction or precipitate with a small concentration of stannous ion, but none with either stannic, ferrous or ferric ion; or (b) a color or precipitate with ferrous ion, but no reactions with either ferric, stannous or stannic. The rates at which all possible reactions take place would also be of as much importance as their equilibrium constants.

A third method of recognizing the end points of oxidizing-reducing processes, which is more general in its application, is an electro-metric process similar to that used in the titration of acids



with bases. It can be calculated from the data on page 348 that in the titration of ferric with stannous ion the ferric-ferrous potential changed from 0.684 volt, when 90 per cent of the needed stannous ion had been added, to  $+0.334$  volt when all of it had been added. Similarly the value of the stannous-stannic potential changed from  $-0.684$  to  $-0.34$  volt. Obviously the rate of change in potential in both processes during the latter part of the titration is large and it is easy to show by a number of simple calculations that it approaches a maximum value as the percentage of added stannous salt approaches that theoretically required and is at a minimum when one-half the necessary amount has been added.

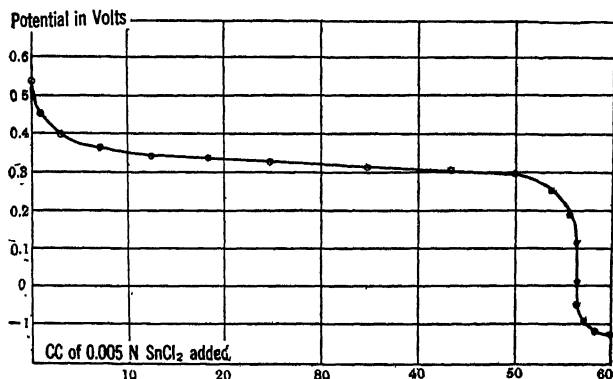


Fig. 60.

These changes in potential may be ascertained by introducing into the solution being titrated a bare platinum wire, which immediately acquires a charge, and a calomel electrode, and measuring the potential of the resulting cell. This measurement gives the potential due to change of ferric to ferrous ion and metallic mercury to mercurous ion, but as the latter has a constant value the measured potential changes with the ratio of ferrous to ferric ion. It is possible that other changes, such as change of stannic to stannous ion, might take place, but since the largest positive  $E_0$  value is the ferric-ferrous change and the largest negative value is the mercury-mercurous ion change these would predominate until concentration of ferric ion became very small or that of stannic ion very large.

In practice it is found that the actual form of the curves representing the change in potential during the progress of the titration is greatly affected by a number of factors in addition to concentration, such as the treatment which the platinum wire used has received. The procedure followed in using this method is to first ascertain the form of the curve for the titration desired representing the change in voltage just before and just after the true end point has been reached. The curve for the titration of ferric ion by stannous<sup>1</sup> ion is shown in Fig. 60. The end point at 50.6 cc. coincides with the point on the curve which is midway between the points of greatest inflection. The true end point for the titration of an unknown solution may be ascertained by plotting that part of the curve at which these inflections occur and locating on it the midway point or by titrating until the combination shows the voltage previously found for this point. This method of determining end points has many advantages.

### Questions and Problems. Series 26

1. Assuming that the potential of the permanganate-hydrogen-manganese ion electrode is +1.483 volts, if all concentrations are molal, what is its value when permanganate and manganous ion are molal and hydrogen ion is 0.001?

*Ans.* 1.200 volts.

2. It is found that the complete reduction of ferric ion by the use of sulfur dioxide requires that the concentration of hydrogen ion be kept within certain limits; explain why.

3. A mixture containing one equivalent of titanous and one of stannic ion is allowed to attain equilibrium; what is the value of the ratio between stannous and stannic ion assuming the  $E_0$  values are - 0.13 and + 0.37 volt? What is the potential of the titanic-titanous and the stannous-stannic electrodes in the equilibrium mixture?

*Ans.*  $4.5 \times 10^6$  and - 0.036 volt.

4. A certain mixture, which has a volume of 1000 cc., contains 0.2 gram  $\text{FeCl}_2$ , 0.2 gram  $\text{FeCl}_3$ , 2.0 grams  $\text{KI}$  and 0.2 gram of  $\text{I}_2$ . Assuming that the three salts are completely dissociated, show how to determine by means of a calculation whether iron would be oxidized or reduced.

5. What is the value in calories of the standard free energy for the reaction between stannous ion, permanganate ion and hydrogen ion, assuming all ions in the mixture are at molal concentration.

*Ans.* 155.991 calories.

6. Calculate the normal electrode potential for the cupric-cuprous ion reaction from those for the cupric ion-metallic copper and cuprous ion-metallic copper.

*Ans.* + 0.178 volts.

<sup>1</sup> Hostetter and Roberts, Jour. Am. Chem. Soc. 41, 1353 (1919).

## CHAPTER XXXIV

### ✓DETERMINATIONS WITH SOLUTIONS OF POTASSIUM PERMANGANATE

#### I. Preparation and Standardization of Solutions

**Peculiarities of Permanganate Solutions.** The fact that permanganate ion, especially in an acid solution, is an unusually effective oxidizing agent, and that it can be employed in many titrations without an indicator or any special device for recognition of the end point, has been discussed on pages 350 and 352. Neutral solutions of soluble permanganates show but little tendency to undergo spontaneous decomposition if kept free from organic matter and away from strong light. It has been shown, however, that the very small quantities of organic matter frequently present in distilled water are slowly oxidized by such solutions and that the resulting precipitate of manganese dioxide catalyzes the reaction by which further quantities of permanganate are reduced. It is found that most preparations of solid potassium permanganate, which is the salt commonly used for the preparation of permanganate solutions, when dissolved in pure water and allowed to stand, yield an appreciable amount of manganese dioxide when filtered. This may be derived from small amounts of manganese dioxide present in the solution from which the salt crystallized or to a slight amount of spontaneous decomposition of the permanganate at the surface of the crystals. The proper procedure for the preparation of a standard solution whose strength will not vary during a period of several months is to dissolve the salt in water which is as pure as can be easily obtained, allow the solution to stand till the organic matter has been oxidized as completely as it can be oxidized by permanganate ion, filter out the resulting manganese dioxide precipitate, and preserve the solution in per-

fectly clean bottles. Filtration should be made by use of an asbestos filter since cellulose slowly reduces permanganate ion and it is impossible to prevent small amounts of cell fibers from being detached from the filter and added to the solution. The presence of hydrogen ion greatly increases the rate of spontaneous decomposition of permanganate ion, but hydroxyl ion favors the formation of manganate ion and manganese dioxide.

**Concentration of the Standard Solution.** The most desirable strength of a standard solution of potassium permanganate is fixed to a large extent by the sensitiveness of the procedure used for the determination of the end point and therefore by the colorific power of the permanganate ion. The error in the determination of the end point with a one-tenth normal solution, namely a solution which contains one-fiftieth of a mole per liter, is in general much less than that involved in the measurement of the solution used. However, if care is taken to keep the volume of the solution titrated small, very satisfactory results can be obtained by using a one one-hundredth normal solution, and such solutions are frequently made use of in titrating small amounts of certain reducing agents. The value of a "tenth normal" solution of potassium permanganate is usually understood to mean the value given above, which assumes that the concentration of hydrogen ion in the solution titrated is large enough to insure reduction of all the permanganate ion used to manganous ion rather than manganese dioxide. If such solutions are used in titrations in which all the permanganate ion is reduced to manganese dioxide it becomes necessary to assume that for these titrations the solution is 0.06 normal in calculating the results obtained. If, for example, a "tenth normal" solution of permanganate is used in oxidizing manganese ion to manganese dioxide 1 cc. of the solution must equal

$$\frac{54.93}{2 \times 1000} \times \frac{1}{10} \times .6 = 0.001648 \text{ gram.}$$

**Necessary Conditions for Titration.** Some judgment must be exercised in deciding upon the character and concentration of the acid which should be present in order that all of the permanganate should act with an equivalency of five. Nitric acid is usually

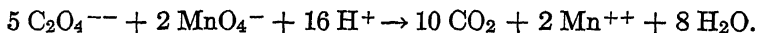
avoided since the nitrate ion may itself oxidize some of the substances in the solution which is being titrated, especially if the temperature and concentration are high. Organic acids are also avoided since some of them are more or less completely oxidized by permanganate ion, and large concentrations are necessary in order to yield the necessary concentration of hydrogen ion. The halogen acids are also objectionable since the halide ions, especially iodide and bromide ion, reduce permanganate ion, causing loss in oxidizing power through volatilization of the liberated halogen, and giving very poorly defined end points. The action of permanganate ion on chloride ion is rather slow at ordinary temperatures, but its rate is increased by the presence of certain other ions, especially ferric ion, and decreased by others, such as manganese ion. It is possible by reducing the temperature, adding manganese ion and greatly increasing the volume of the solution being titrated, to reduce the errors involved in the titration of ferrous ion in the presence of chloride ion to negligible proportions if the concentration of chloride ion is very low. It is preferable, however, to avoid such titrations.

Assuming that sulfuric acid is used to introduce the needed concentration of hydrogen ion the amount added should be sufficient to prevent the separation of manganese dioxide (see page 350), but not large enough to lead to the production of oxygen (or ozone), owing to the spontaneous decomposition of permanganic acid or manganese heptoxide. The minimum amount needed depends somewhat upon the substances being titrated. In the titration of ferrous or stannous ion 1 cc. of concentrated sulfuric acid per 100 cc. of solution, which gives  $(H^+)$  a value of about 0.35 N, will suffice, but in the titration of less powerful reducing agents larger concentrations are needed. If the amount of acid reaches a value of 40 cc. per 100 of solution oxygen begins to be liberated, and even at much smaller concentrations there is a slow decomposition of permanganate ion into manganese dioxide, which gives rise to a considerable degree of uncertainty in the determination of the end point. A sufficient and safe amount of acid to use for most titrations is 5 cc. per 100 cc. of solution.

**Choice of Method of Standardization.** The statements in the first paragraph of this chapter show that it is not possible

to prepare an accurately standardized solution of permanganate ion by weighing out the proper amount of the potassium salt of permanganic acid, dissolving and diluting to a calculated volume. It must be standardized by oxidizing against a weighed amount of some primary standard. The substances which have been used for the purpose include ferrous ammonium sulfate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ ), metallic iron prepared electrolytically, oxalic acid,  $(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ , and sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ . Of these, preference is to be given to the last because the details of the procedure for the preparation of the pure salt have been carefully determined,<sup>1</sup> and it is now prepared commercially for this special purpose. Samples of guaranteed purity are also to be had from the Bureau of Standards at Washington.

**Peculiarities of the Reaction between Oxalate and Permanganate Ions.** If permanganate ion is added to a solution containing hydrogen and oxalate ions at room temperature decoloration of the solution takes place very slowly at first. If heated to  $80^\circ \text{C}$ . the process is somewhat faster even at the outset and soon becomes practically instantaneous. If equivalent amounts of the two reagents are used the oxalate is completely oxidized to carbon dioxide and the permanganate is almost completely reduced to manganous ion in accordance with the expression



Since the solubility of carbon dioxide in the solution, when calculated to moles per liter, is extremely small, this reaction should be nearly complete. There is no experimental evidence that the reverse process takes place even when the concentration of carbon dioxide is large. It has been shown, however, that very small but measurable amounts of some oxidizing agent, which is not permanganate ion, is present in the solution when equivalent amounts are present. Another peculiar feature of the reaction is that if manganous ion is present at the outset the delay in the decoloration of the solution is greatly reduced. Evidently manganese ion catalyzes the process and the reaction is autocatalytic. These facts suggest that the reaction is more complex than the preceding

<sup>1</sup> Blum, Jour. Am. Chem. Soc., 34, 123 (1912).

equation indicates and that although this equation correctly represents the entire process the reaction actually involves one or more stages. There is no evidence of more than one stage in the oxidation of the carbon of the oxalate ion, but there is some evidence that the reduction of the permanganate ion involves formation of either trivalent or tetravalent manganese as an intermediate step. Tetravalent manganese is known only in the very slightly soluble hydrated dioxide and certain slightly soluble compounds of this with bases, which are by some supposed to be salts of manganic acid,  $\text{H}_2\text{MnO}_3$ . The trivalent manganese is known to exist as the ion  $\text{Mn}^{+++}$  in small concentrations only but it forms complex ions with oxalic acid and a number of other substances which are more stable. Several schemes, representing the actual mechanism of the entire process, based upon the assumption that the trivalent and tetravalent manganese are intermediate products, have been suggested, but that outlined by Skrabal<sup>1</sup> is based upon the largest amount of experimental evidence. The essential features of his theory, omitting for sake of simplicity a number of subsidiary reactions, are expressed by the following reactions:

- (1)  $2 \text{C}_2\text{O}_4^{--} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow \text{Mn}^{+++} + 4 \text{CO}_2 + 4 \text{H}_2\text{O}$  (slow)
- (2)  $2 \text{Mn}^{+++} + \text{C}_2\text{O}_4^{--} \rightarrow 2 \text{Mn}^{++} + 2 \text{CO}_2$  (very rapid)
- (3)  $4 \text{Mn}^{++} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow 5 \text{Mn}^{+++} + 4 \text{H}_2\text{O}$  (rapid)

If (1) is a slow reaction but little permanganate ion will be used up for an appreciable time interval, unless the solution also contains manganous ion which by (3) at once yields manganic ion and the latter by (2) at once oxidizes oxalate ion to carbon dioxide. If manganous ion is present at the outset the delay necessary for the formation of manganic ion by (1) is avoided. When most of the oxalate ion has been used up the rate of (2) and therefore of (3) falls off and slightly more than the theoretically needed amount of permanganate must be added to yield an amount of manganic ion required by (3) and to give a recognizable color to the solution.

<sup>1</sup> Skrabal, Z. anorg. Chem., 42, 1 (1904).

✓ **Standard Procedure for the Titration of Oxalate Ion by Permanganate Ion.** The correction for the excess of permanganate ion needed for the oxidation of oxalate ion is usually slight and is frequently disregarded. It may be determined by simply finding out what volume of permanganate solution must be added to a mixture containing the same amount of water and sulfuric acid as the oxalate solution being titrated. It is clear that if the permanganate solution is used for the titration of oxalate ion only, and if the amounts of oxalate titrated are always the same, all the results will be affected by the same percentage error and no corrections will be necessary. Usually, however, the same permanganate solution is used for the titration of different substances, and the volume used in every titration made should be corrected.

A second error to be looked for in all titrations in which permanganate ion is used in an acid solution is a loss of oxidizing power, and therefore excessive consumption of permanganate, from the spontaneous decomposition of permanganic acid and the liberation of oxygen. This is, in general, a very slow process but its rate may become large enough to cause appreciable errors under certain conditions. These conditions include a large concentration of hydrogen ion, a high temperature, and an accumulation of a large excess of permanganate ion in the solution during titration owing to imperfect stirring. The conditions necessary to reduce this error to a minimum have been determined by McBride<sup>1</sup> and are given in detail in the following paragraph. He concluded that under these conditions the total error of the titration should be expected to vary between one part in one thousand and one part in two thousand.

**Procedure for the Preparation and Standardization of Standard Permanganate Solution.** Weigh out 6.4 grams of pure crystallized potassium permanganate into a 400-cc. beaker; add 250 cc. of water; heat to about 60° C., and stir for a few minutes; decant off most of the clear liquid into a 2000-cc. flask; again add water, heat and stir, and decant the clear liquid; continue this cycle of operations until all of the salt has been dissolved. Although the salt is highly soluble its rate of solution is slow, and time can be

<sup>1</sup> McBride, Jour. Am. Chem. Soc., 34, 415 (1912).



saved by proceeding as directed. Finally dilute to 2000 cc. and allow to stand for at least twenty-four hours. This should insure oxidation of any organic matter in the solution, in so far as it can be oxidized by the permanganate. Next prepare an asbestos filter and connect with a 2-liter bottle which has been carefully cleaned by digestion, first, with hydrochloric acid, and second, with cleaning mixture, and which has been rinsed with several portions of distilled water, as shown in Fig. 57, and filter the permanganate solution through it. Keep the solution in a dark closet or cover with opaque paper. Dry some pure sodium oxalate for a half hour at  $150^{\circ}\text{C}$ . Weigh out from 0.25 to 0.30 gram into a 400-cc. beaker, dissolve in 200 cc. of water, add 30 cc. of six normal sulfuric acid, heat to  $90^{\circ}\text{C}$ ., and titrate at once with the permanganate solution, stirring vigorously after each addition. The rate of addition should not exceed 10 to 15 cc. per minute during any part of the titration, and after the permanganate color begins to fade out slowly, which is usually during the addition of the last cubic centimeter, only one drop should be added at a time. The titration should be carried to the point at which the mixture shows a very slight but definite pink color that is permanent for at least five minutes.

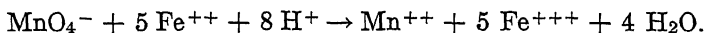
Titrate in a similar manner a mixture containing the same volumes of water and acid as the oxalate solution and subtract the volume thus found from that used in the oxalate titration. Calculate the normality of the solution by dividing the weight of sodium oxalate oxidized by 1 cc. of the solution by the number of grams present in 1 cc. of a normal solution, assuming that the equivalency of sodium oxalate is two.

## II. Determination of Iron in Cast Iron

**Composition of Samples.** Cast iron usually contains several per cent of silicon and carbon, and smaller amounts of manganese, sulfur and phosphorus. If dissolved in sulfuric acid the silicon forms silicic acid, the manganese forms manganous sulfate, the phosphorus forms phosphoric acid, and that part of the carbon which is present in the form of graphite separates as such, but the carbon which is present as iron carbide ( $\text{Fe}_3\text{C}$ ) yields more or less

volatile hydrocarbons. Even if the resulting solution is heated to boiling it will be found to reduce more permanganate than would correspond to the iron present owing to the reducing action of these hydrocarbons. The simplest method of avoiding this error is to destroy these reducing substances by a preliminary treatment with potassium permanganate, reduce the iron necessarily oxidized by this treatment, and again titrate with the permanganate solution. If a slight excess of permanganate is used and the solution heated during the preliminary oxidation, a more complete oxidation of these reducing substances than would be effected in the final titration is assured. Experience shows that the products formed are not reduced by the method used for the reduction of the iron. An alternative method is to dissolve the sample in a small amount of nitric acid, displace the latter completely by evaporating till fumes of sulfur trioxide appear, and redissolve in water. This treatment insures more complete oxidation than the permanganate treatment, but necessitates great care in expelling the last traces of nitrate ion before the iron is reduced.

**Oxidation of Ferrous Ion by Permanganate Ion.** The oxidation of ferrous ion by permanganate ion in the presence of hydrogen ion is represented by the equation

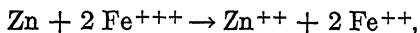


The sum of the potentials of the two half-cell reactions concerned, assuming all ions are at molal concentrations, is 0.74 volt. This is of little significance, however, because the reaction is not a reversible one. Unlike the oxidation of oxalate ion by permanganate ion the reaction is practically instantaneous, even at ordinary temperatures, and the concentration of hydrogen ion needed to prevent the separation of manganese dioxide is less than that needed in the oxalate titration. It is easy to show by a simple experiment that the reaction is slightly less complete if ferrous ion is added to permanganate ion than if this order is reversed, and all titrations should be made by the former procedure.

The end point of the titration differs slightly from that for the oxalate titration owing to the fact that the pink color due to the

slight excess of permanganate ion is modified to some extent by the yellow color of the ferric ion formed. The method possesses a higher degree of accuracy than any of the other methods used for the determination of iron.

**Methods of Reducing Iron.** The method used to reduce ferric ion, before titration with permanganate, must insure complete reduction of the former, and no other substances which reduce permanganate should be left in the solution. Solid reagents, the excess of which can be removed by filtration, or gaseous reagents, the excess of which can be driven off by heating, are most largely used. Of the solids metallic zinc, aluminum, magnesium, or lead are best. The reactions concerned correspond to such equations as



and even with such a metal as lead are practically complete. Reduction with these reagents is always effected in a solution strongly acidified with sulfuric acid, but the hydrogen which is also produced has no effect upon the degree of oxidation of the iron, and reduction takes place only at the surface of the metal used. Excessive action of the acid on the metals is to be avoided since it may lead to mechanical losses. This can be greatly reduced by amalgamation, that is, by allowing the zinc to stand in a dilute solution of mercurous salt until a coating of metallic mercury has been formed on its surface. Although this decreases the reducing potential of the zinc by reducing its concentration it is still able to effect practically complete reduction of the iron. Care must be taken to obtain samples of metals which are themselves free from iron.

Of the gaseous reducing agents, hydrogen sulfide, which is oxidized by ferric ion to sulfur and water, and sulfur dioxide, which is oxidized to sulfuric acid, are largely used. Both reagents reduce the iron rapidly and completely, provided the concentration of hydrogen ion in the solution is kept below a certain maximum value. Boiling the solution for a few minutes completely expels the excess used. The finely divided sulfur, which is formed when hydrogen sulfide is used, is without appreciable effect upon the permanganate solution unless the mixture titrated is hot.

**Use of the Jones Reductor.** Since reduction takes place only at the surface of the metal used the process is a slow one, especially if the solution has a large volume. However, if the metal is reduced to a fine state of division and the iron solution passed slowly

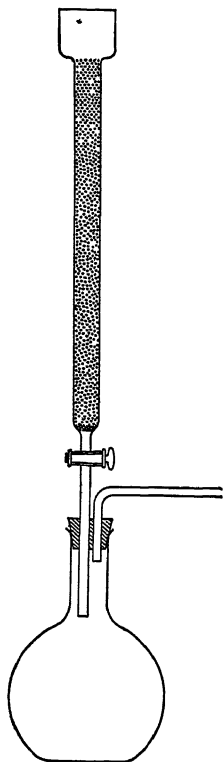


Fig. 61.—Jones reductor.

through a tube filled with it, both the total amount of metal consumed and the time required for complete reduction are very greatly decreased. This principle is made use of in the Jones reductor represented in Fig. 61. Its use may easily reduce the time needed for complete reduction from several hours to ten minutes. It is customary to prevent air from coming into contact with the metal while the solution is being reduced, as it was formerly supposed that a small amount of hydrogen peroxide, subsequently oxidized by the permanganate, may be formed under these conditions, but the supposition is not confirmed by recent experiments.<sup>1</sup>

**Outline of Method of Procedure.** Prepare the sample either by drilling out 10 grams of powder or turning off an equal amount of thin shavings in a lathe from the metal to be analyzed, and mixing. Weigh out 0.25 gram of the sample into a 200-cc. beaker, add 25 cc. of dilute sulfuric acid, warm gently, and allow to stand until no more hydrogen is evolved and only gelatinous silicic acid and graphite, which float in or on the solution, remain. Add sufficient permanganate solution to impart a deep red color to the

mixture even after it has been warmed to 50° C. Dissolve the precipitate of manganese dioxide, which usually separates, by slowly adding the smallest possible amount of sodium sulfite. If left in the solution this precipitate may occlude small amounts

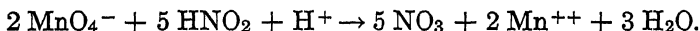
<sup>1</sup> Burdick, Jour. Am. Chem. Soc., 48, 1179 (1926).

of iron and cause low results. The solution must be heated long enough to expel completely the excess of sulfur dioxide left in it. Filter off the residual graphite and separated silica, using a 9-cm. filter and washing till shown to be free from iron. Endeavor, however, to keep the total volume less than 100 cc.

Prepare a Jones reductor as follows: Dissolve 5 grams of metallic mercury in 50 cc. of dilute nitric acid and dilute to 250 cc. Add 250 grams of granulated zinc, fine enough to pass a 20-mesh but not a 30-mesh sieve. Stir the mixture for a few minutes, then pour off the solution and wash the residual metal till free from nitrate ion. Place a dish of perforated platinum foil in the bottom of a reductor tube, cover this with a thin layer of glass wool, and finally fill with the amalgamated zinc as far as the cup-like enlargement at the top. Connect the tube with a filter flask by means of a rubber stopper and the flask with a suction pump. Rinse out the tube by passing through it 250 cc. of sulfuric acid, made by diluting 20 cc. of six normal acid to 250 cc. Next pass the iron solution through the reductor, regulating the pump so as to require about fifteen minutes for the passage of the entire solution, and as soon as the latter has been drawn down to the top of the zinc in the tube, rinse out the tube, using 200 cc. of dilute sulfuric acid. Detach the flask from the reductor tube and titrate the solution without delay. Titrate an equal volume of dilute acid with the permanganate and subtract the amount found from that used in the actual titration. Calculate and report the percentage of iron present in the sample.

### ✓ III. Determination of Nitrites in Commercial Salts

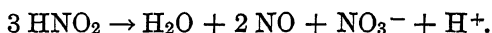
**Oxidation of Nitrous Acid.** The oxidation of nitrous acid by permanganate and hydrogen ion is represented by the equation:



This reaction takes place in the direction indicated at a high rate of speed until the concentration of nitrous acid has been reduced to a small value; the rate then decreases rapidly and it is not possible to determine with even approximate accuracy the end point

of the process. There is no evidence to show that the reverse process takes place, and the results of the various attempts to measure the potential of the nitrous acid-nitric ion half-cell reaction are of questionable value. It is easy to prove by titration of known amounts of nitrous acid with permanganate that the reaction given can be made practically complete and instantaneous if a moderate excess of permanganate is made use of. The excess can then be determined by titrating the resulting mixture with a standard solution of an appropriate reducing agent, and, if a known amount of standard permanganate was used, that portion of it which was actually reduced by the nitrous acid can be found by subtraction. This is an illustration of the device known as "back titration." (See page 261.) It is clear that the reducing agent used to titrate the excess of permanganate added should not be oxidized by the nitrate ion in the solution. This requirement is fulfilled by a solution of ferrous ion provided the mixture is kept cold and has a sufficiently low concentration of nitrate ion and hydrogen ion.

**Spontaneous Decomposition of Nitrous Acid.** Nitrous acid is a very weak acid and even in solutions of small concentration decomposes in agreement with the expression:



The rate of decomposition is fairly large even at ordinary temperatures and is greatly increased by a moderate rise in temperature and by a number of catalysts. The small concentration of hydrogen ion needed for the oxidation of salts of nitrous acid by permanganate ion is more than sufficient to cause large losses of nitrous acid through the decomposition unless care is taken to add an excess of permanganate to the solution to be titrated before it is made acid. Even then care must be taken to use dilute acid, to add it slowly, and to stir vigorously during the oxidation. Solutions of soluble nitrites also undergo a similar decomposition corresponding to the equation:



Another possible source of error in the titration of nitrites is the direct oxidation of nitrite to nitrate ion by atmospheric oxygen;

if this error is to be eliminated such solutions must be titrated as soon as prepared, or preserved in flasks in which air has been displaced by carbon dioxide.

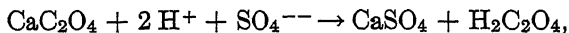
**Composition of Commercial Samples.** The nitrites of both sodium and potassium are very soluble and extremely hygroscopic. The commercial forms commonly sold consist of either coarse crystals or sticks of small diameter both of which are usually moist and sticky. As it is very difficult to crush and mix such samples, and water is rapidly absorbed during the process, it is not easy to secure a representative sample. The uncertainties concerned are best avoided by weighing out a large amount of sample, dissolving and diluting to a known volume and taking a fractional part of the solution for the actual titration. Good commercial samples should contain at least 90 per cent of the salt concerned, the residual percentage being made up of water and small amounts of nitrates, chlorides, sulfates and hydroxides. Complete evaluation of samples sold as potassium nitrite would require a determination of the potassium also.

**Detailed Outline of the Method of Procedure.** Prepare a solution of ferrous sulfate by dissolving 7 grams of the crystallized salt,  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , in water, adding 20 cc. of dilute sulfuric acid, and diluting to 250 cc. This solution should be preserved in a stoppered flask. Determine the volumetric relation between this solution and the standard permanganate solution by diluting 25 cc. of it to 200 cc., adding acid, and titrating with the permanganate. Weigh out about 2 grams of the well-mixed sample of the nitrite in a weighing bottle, dissolve and dilute to 250 cc. in a graduated flask, and mix thoroughly. Transfer 25 cc. of this solution to an Erlenmeyer flask, add exactly 75 cc. of the permanganate solution, and then slowly introduce 5 cc. of six normal sulfuric acid, being careful to prevent accumulation of the acid in any part of the solution. The resulting mixture should contain an excess of permanganate and should show an intense pink color, although this may be modified by the manganese dioxide which sometimes separates. Next add exactly 25 cc. of the ferrous sulfate solution, or, if this is not sufficient to decolorize the solution and dissolve any separated manganese dioxide, add a further measured quantity of the ferrous sulfate solution. Finally titrate

the mixture with the permanganate solution. Calculate the volume of permanganate solution equivalent to the ferrous sulfate solution used and subtract from the total volume of permanganate added. Calculate from the volume thus found, from the weight of sample actually titrated, from the normality of the permanganate solution, and from the equivalency and molecular weight of the nitrite, the percentage present in the sample.

#### IV. Determination of Calcium in Limestone

**Theory of the Method.** An extremely useful indirect method for the determination of calcium is based upon the insolubility of calcium oxalate and upon the accuracy with which oxalic acid can be determined by titrating with a solution of permanganate ion. The accuracy of the procedure depends, first, upon the accuracy with which calcium can be separated as oxalate from solutions containing associated elements; second, upon the completeness of the reaction,



and third, upon the completeness of the reaction representing the oxidation of oxalic acid. The first of these factors has been discussed on page 215. It is there shown that, even in the presence of moderate amounts of magnesium, the error involved in this separation can be made very small. The conversion of calcium oxalate into calcium sulfate is determined in part by the relative solubilities of the two solids, and in part by the relative values of the dissociation constants of sulfuric and oxalic acids. Furthermore, the reaction must ultimately be practically complete owing to the decrease in the concentration of the oxalic acid by conversion into carbon dioxide and water during the last step in the process. A somewhat higher degree of accuracy can be attained in the titration of a precipitate of calcium oxalate than in igniting and weighing it.

**Detailed Outline of the Method of Procedure.** Weigh out 0.5 gram of sample into a 250-cc. beaker, cover with a watch glass, introduce 10 cc. of dilute hydrochloric acid and 5 cc. of dilute nitric acid, and warm on a steam or sand bath until decomposition



of the sample seems to be complete. Rinse off and remove the watch glass cover, and dilute to about 100 cc. Heat the solution nearly to boiling, add a slight excess of ammonium hydroxide, digest for a few minutes, then filter on a 9-cm. filter, and wash till free from chloride ion. If the volume of iron and aluminum hydroxides thus obtained is large, redissolve in the smallest amount possible of warm dilute hydrochloric acid, dilute the resulting solution to 50 cc., precipitate with ammonium hydroxide as before, filter, and combine this filtrate with that first obtained.

Dilute the combined filtrate to 300 cc., and add a drop of methyl orange indicator and sufficient dilute hydrochloric acid to cause the solution to assume a pink rather than a yellow color. Heat to boiling, add 18 cc. of oxalic acid solution, and stir for a few minutes; if a precipitate does not separate add single drops of normal ammonium hydroxide, stirring vigorously after each addition, until the precipitate begins to separate. After about ten minutes add dilute ammonium hydroxide, slowly and with constant stirring, until the solution is distinctly alkaline. Finally allow the mixture to stand for at least half an hour.

Filter off the precipitate on a 9-cm. filter and wash both precipitate and filter very thoroughly, that is, until 20 cc. of the washings, acidified with sulfuric acid and heated to 80° C., do not decolorize a drop of tenth normal permanganate solution. Remove the filter from the funnel, open it out, and flatten against the side of a 400-cc. beaker. Rinse the precipitate adhering to the filter into the bottom of the beaker and bring the total volume up to 200 cc. Add 30 cc. of dilute sulfuric acid, heat to 80° C., and titrate with the permanganate solution as in the standardization of the solution. Calculate and report the percentage of calcium oxide present, noting that, since one atom of calcium yields 1 molecule of oxalic acid, the equivalency of the calcium equals that of oxalic acid, namely two.

#### ✓ V. Possible Uses of Solutions of Permanganate Ion

**Summary of Permanganate Processes in Use.** The large value of the electrode potential corresponding to the permanganate ion-manganese ion reaction, together with the fact that with many

reducing agents the reverse process does not take place, makes it possible to use solutions of permanganate ion for the determination of many substances. The accuracy of these processes varies greatly, but all of those included in the following list, which is far from being complete, are satisfactory quantitative processes. They are grouped under the following four heads:

First, the direct oxidation in an acid solution of certain metallic elements, namely iron, when oxidized from di- to trivalent; tin, when oxidized from di- to tetravalent; copper, when oxidized from mono- to divalent; molybdenum and tungsten, when oxidized from tri- to hexavalent; titanium, when oxidized from tri- to tetravalent; uranium, when oxidized from tetra- to hexavalent; vanadium, when oxidized from either di- or tetravalent to pentavalent; and manganese, which is oxidized in a neutral solution from di- to tetravalent manganese.

Second, the direct oxidation in an acid solution of certain inorganic acids or their ions, namely: nitrous acid, which is oxidized to nitric; sulfurous acid, which is oxidized to sulfuric; hydrogen sulfide, which is oxidized to sulfur and water; ferrocyanic acid, which is oxidized to ferricyanic acid; sulfoeyanic acid, which is oxidized to hydrocyanic and sulfuric acids; and hydrogen peroxide, which is oxidized to oxygen and water.

Third, the direct oxidation in acid solution of certain organic substances, namely: oxalic and formic acids, and tannin.

Fourth, a large number of indirect determinations. These include elements which form insoluble compounds of definite composition with the acids enumerated in the second and third groups. Such compounds can be separated from the solution, purified by washing, decomposed by means of a stronger acid, and the acid then liberated titrated with the permanganate solution. Of especial interest is a method largely used for the determination of phosphorus in iron alloys. It involves the separation of molybdenum as ammonium phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MnO}_3$ , redissolving and reducing the molybdenum to trivalent form by metallic zinc, and titration of the molybdenum with permanganate, which reoxidizes it to the hexavalent form.

## VI. Questions and Problems. Series 27

1. What elements have atomic numbers near that of manganese? What differences and what resemblances are there between the chemical properties of manganese and these elements?

2. What changes in the structure of the manganese atom are believed to be associated with the different stages of oxidation exhibited by manganese-containing compounds?

3. Write the expression representing the equilibrium which exists in solution between potassium permanganate, potassium manganate and manganese dioxide. What use can be made of this reaction commercially? Why is it that in discussing the use of permanganate ion in volumetric analysis the possibility of the formation of manganate ion is ignored?

4. What would you expect to take place when solid potassium permanganate is heated in an open crucible to  $600^{\circ}\text{C}$ ? How would you test experimentally the correctness of your assumption? What oxide of manganese is formed when the dioxide is heated above  $600^{\circ}\text{C}$ . in an open crucible?

5. What is the equivalency of (a) nitrate ion when reduced to nitrite ion, (b) persulfate ion ( $\text{S}_2\text{O}_8^{--}$ ) when reduced to sulfate ion, (c) vanadate ion ( $\text{VO}_3^-$ ) when reduced to vanadyl ion  $\text{VO}_2^{++}$ , (d) ferricyanide ion when reduced to ferrocyanide ion?

6. What weights of (a)  $\text{Ba}(\text{NO}_3)_2$ , (b)  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , (c)  $\text{KVO}_3$ , (d)  $\text{K}_3\text{Fe}(\text{CNO})_6$  should be present in a liter of a normal solution of these reagents, assuming that the reactions suggested in the preceding question take place?

7. What weight of  $\text{KMnO}_4$  should be present in a liter of solution in order that each cubic centimeter should represent 0.005 gram of (a)  $\text{FeO}$ , (b)  $\text{Fe}_3\text{O}_4$ , (c)  $\text{Fe}$ , assuming that the iron is oxidized to the ferric state from the form represented by these substances? *Ans.* (a) 2.2005, (b) 0.6826, (c) 8.4898.

8. The zinc in a sample of impure metal is dissolved, without the liberation of hydrogen, in an acid solution of ferric sulfate, and the resulting solution titrated with a standard solution of potassium permanganate. If the sample used weighed 0.4811 gram, the permanganate solution is 0.3410 normal, and 42 cc. of it are used in the titration, what percentage of zinc must be present? How would the result obtained differ from the correct per cent of metallic zinc actually present if the sample contained (a)  $\text{ZnO}$ , (b)  $\text{Fe}$ , (c)  $\text{Cu}$ ? *Ans.* 97.31.

9. What is the equivalency of (a) zinc, when precipitated as  $\text{ZnS}$  and titrated with permanganate solution, (b)  $\text{Cu}$ , when precipitated as  $\text{CuCNS}$  and titrated with permanganate, (c) phosphorous, when precipitated as  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MnO}_3$ , the  $\text{Mn}$  reduced to  $\text{Mn}_{24}\text{O}_{37}$  and titrated with permanganate solution? *Ans.* (a) 2, (b) 7, (c) 35.

10. In determining the iron in an iron alloy, as outlined on page 364 (a) why dissolve in  $\text{H}_2\text{SO}_4$  rather than in  $\text{HCl}$  or  $\text{HNO}_3$ ? What would take place if (b) the sulfuric dioxide was not expelled before passing the solution through the reductor? (c) if the sulfuric acid used in rinsing out the reductor con-

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tained small amounts of  $\text{HNO}_3$ ? If the sample contained small amounts of (d) Cu, (e) Mn, (f) Ni, (g) Cr?

11. In determining calcium in limestone as outlined on page 368 (a) is there any objection to dissolving in  $\text{HNO}_3$  or in  $\text{H}_2\text{SO}_4$  rather than in  $\text{HCl}$ ? (b) Would you expect the presence of small amounts of manganese or strontium in the sample to affect the result? (c) Why should care be taken to keep the concentration of acid used to dissolve the precipitated oxalate small?

12. Calculate the electromotive force and the free energy due to the reaction between metallic iron and a solution in which  $(\text{Cu}^{++})$  is 0.01 and  $(\text{Fe}^{++})$  is 0.001.

*Ans.* 0.843 volts and 38,877 calories.

13. If the system described in the preceding problem is allowed to attain equilibrium what will the ratio of  $(\text{Fe}^{++})$  to  $(\text{Cu}^{++})$  be?

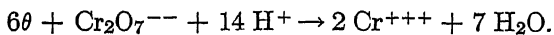
*Ans.*  $1 \times 10^{26.58}$ .

## CHAPTER XXXV

### ✓ DETERMINATIONS WITH SOLUTIONS OF POTASSIUM DICHROMATE

#### I. General Features of the Process

**Dichromate Ion as an Oxidizing Agent.** Solutions of soluble dichromates are, in the presence of hydrogen ion, strong oxidizing agents. Most of the chromium in such solutions is in the form of the dichromate ion,  $\text{Cr}_2\text{O}_7^{--}$ , but owing to hydration small concentrations of  $\text{HCrO}_4^-$  and still smaller concentrations of  $\text{CrO}_4^{--}$  are present. The chemical activity of such solutions is due for the most part to the reaction expressed by the equation:



Since the process does not readily reverse, the value of the corresponding electrode has not been determined, but it is easy to show that the ability of the dichromate ion to oxidize certain reducing agents is only slightly less than that of the permanganate ion. Since a larger number of hydrogen ions are used up, its oxidizing potential increases greatly with increasing  $(\text{H}^+)$ . Unlike the permanganate ion it does not oxidize chloride ion unless  $(\text{H}^+)$  is large and the temperature above  $20^\circ$ ; therefore, it is possible to make determinations in which chloride ion is present in moderate concentrations with but little danger of loss of oxidizing power due to the formation of chlorine gas. Additional advantages of the dichromate solution are that it can be kept without appreciable deterioration for months and that, since potassium dichromate is readily obtained in a high degree of purity and is not appreciably hygroscopic, it can be used as a primary standard.

**Determination of End-points.** When solutions of dichromates are reduced the orange red color due to dichromate ion is changed first to mixtures of red and green and finally to the pure green of

trivalent chromium ion. The point at which the reduction is complete is not recognizable by direct observation. The best indicator thus far suggested is diphenyl amine, which is oxidized by a slight excess of dichromate ion to a dark blue compound which contains a quinoid group. If the electromotive force of this reaction is less than that representing the oxidation of the substance being titrated, or if it proceeds at a slower rate, it should be possible to determine the end point with the indicator. Exact information regarding the electromotive force and rate of this reaction is not available but it has been shown<sup>1</sup> that good results can be obtained in the titration of ferrous ion by means of the indicator.

Another procedure for the determination of the end point in the titration of ferrous ion by dichromate ion depends upon the recognition of the point at which all the ferrous ion has been changed into ferric ion. When a solution containing ferricyanide ion is added to a solution containing ferric ion, only a slight increase in the redness of the mixture is noticeable unless the concentration of the ferricyanide ion is too large, but the presence of a small concentration of ferrous ion yields a deep blue or greenish blue precipitate of ferrous ferricyanide (Turnbull's blue). It is possible to recognize the presence of one part of ferrous ion in 100,000 of water by this test. The formation of the ferrous ferricyanide precipitate is not readily reversible and when once formed it persists even after the concentration of ferrous ion has been reduced to a very small value by the addition of an equivalent amount of dichromate ion. It is not possible therefore to use the reagent as an indicator if added directly to the solution but good results are obtainable if used as an "outside" indicator. The accuracy with which the end point is ascertained is not affected by moderate variations in  $(H^+)$ , but it is very important to use a dilute and freshly prepared solution of the indicator. If the solution has been exposed to sunlight for even twenty-four hours, appreciable amounts of ferrocyanide ion are found which give insoluble colored compounds with both ferrous and ferric ion. If the concentration exceeds one-tenth of 1 per cent the color

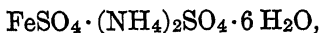
<sup>1</sup> Knop, Jour. Am. Chem. Soc., 46, 263 (1924).

of the indicator solution itself materially affects the accuracy of the process. Furthermore, the size of the drop of indicator solution used, as compared with the size and concentration of the drop of solution which is tested, affects the accuracy. Even those tests which show no reaction for ferrous ion at first, gradually develop a blue color, and therefore a definite time interval should be allowed in judging whether the true end point has been reached.

The electrometric method of determining the end point is found to be extremely accurate and is widely used for this purpose.

**Uses of the Dichromate Solution.** Although a number of metallic ions are completely and rapidly oxidized to a higher valence by dichromate ion its most important use is the titration of ferrous iron. It is peculiarly useful in the analysis of iron ores, most of which are difficult to get into solution without the use of hydrochloric acid. As already noted, the presence of chloride ion causes a large error when ferrous ion is titrated with permanganate ion. A further advantage is that the iron can be reduced, before the titration is made, very rapidly by the use of a solution of stannous chloride. An entire determination of the iron in an easily soluble ore can be made in twenty minutes. Since the dichromate solution is commonly used for the determination of iron only it is convenient to use a solution of such a strength that each cubic centimeter oxidizes 0.005 gram of iron rather than a solution which bears a simple relation to normal strength.

**Procedure for the Preparation and Standardization of a Dichromate Solution.** Weigh out exactly 4.39 grams of pure potassium dichromate, dissolve in water and dilute to exactly 1 liter. Each cubic centimeter of this solution should oxidize 0.005 gram of iron but since there are certain errors in making the titration, etc., its actual value should be checked by titrating against a pure sample of a primary standard. Weigh out 1 gram of pure ferrous ammonium sulfate,



dissolve in 100 cc. of water, add 10 cc. of dilute hydrochloric acid, and titrate at once with the dichromate solution. Prepare the indicator solution by dissolving 0.05 gram of pure potassium ferricyanide in 50 cc. of water. Add at once to the iron solution

26 cc. of the dichromate solution, and then test the mixture for unoxidized iron by bringing a drop of it into contact with a drop of the indicator on a clean porcelain plate. If the test shows an intense blue color, continue adding the dichromate solution in quantities of 0.2 cc. at a time until the test shows a light blue only, then continue adding a drop at a time until the test shows only a clear yellow, which persists for at least one minute. If an excess is used, the tests acquire a slight shade of red. Calculate the weight of iron oxidized by 1 cc. of the solution.

## ✓ II. Determination of Iron in Iron Ores

**Decomposition.** The more easily soluble ores of iron, including siderites, which are mainly ferrous carbonate, and many of the hematites and magnetites, which are mainly ferric oxide and ferrous-ferric oxide respectively, are dissolved by treatment with warm hydrochloric acid. The rate of decomposition is greatly increased by the addition of a small amount of stannous chloride. A very small amount of insoluble residue resulting from treatment with these reagents is usually assumed to be free from iron and disregarded, provided it is of a pure white color; it may contain iron in the form of an insoluble silicate. Many samples of limonite ores, which contain carbonates and sometimes organic matter, and many ores which contain sulfur, dissolve in the hydrochloric acid and stannous chloride only after ignition in an open crucible. This treatment also destroys the organic matter, the presence of which might cause the final result to be high. The more difficultly soluble ores, including many varieties of hematite, magnetite and limonite, and all ores containing iron in the form of an insoluble silicate, are most easily and completely decomposed by fusion with sodium peroxide. This treatment yields ferrates and silicates of sodium, and also aluminates, chromates, and manganates if these elements are present. The excess of sodium peroxide used, and also the chromates and manganates, are completely reduced by heating with hydrochloric acid of sufficient concentration, and any chlorine which may be liberated is either volatilized or is reduced by the stannous chloride used to reduce the iron.



The action of molten peroxide of sodium on platinum crucibles is sufficiently energetic to render their use inadvisable; its action on nickel crucibles is also appreciable, and both nickel and iron, small amounts of which are usually present in the metal of which such crucibles are made, are usually present in the resulting solution in sufficient amounts to produce appreciable errors. Crucibles of silver may be used but well-glazed porcelain ones answer very well, for, although the glaze is gradually disintegrated, no appreciable error is introduced as it is practically free from iron, and a crucible can be used for several analyses.

**Reduction of Ferric Iron by Stannous Ion.** As noted on page 347 ferric ion is almost completely and instantly reduced by stannous ion provided the solutions used are hot and concentrated. Since solutions of ferric chloride when hot possess an intense red or yellow color, whereas solutions of ferrous salts possess a slight greenish color only, the point at which sufficient stannous ion has been added to completely reduce the ferric ion in a solution can be determined with a fair degree of accuracy by noting the color change of the solution. It is difficult, however, to reduce all of the iron in the solution without introducing a slight excess of stannous ion, and since this readily reduces chromic acid the excess must be oxidized before titration with the dichromate solution, without at the same time reoxidizing any of the iron. This can be effected by means of mercuric chloride, which readily oxidizes the tin but not the iron, and is itself reduced to insoluble mercurous chloride, which compound does not reduce chromic acid. If, however, the solution is hot, and if its concentration with respect to stannous ion is large as compared with that of mercuric ion, the reduction may go further and metallic mercury may be formed, which, unlike mercurous chloride, is capable of reducing dichromate ion. Hence care must be taken in the process to add a slight excess of stannous chloride only, to cool and dilute before adding the mercuric chloride, and to add a relatively large amount of the latter. A solution of stannous chloride containing 101 grams of the crystallized salt,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , per liter, 1 cc. of which is capable of reducing 0.05 gram of ferric iron, is a convenient one for this purpose. Such a solution should also contain 100 cc. of concentrated hydrochloric acid per liter

to prevent the separation of an insoluble basic chloride of tin.

**Effect of Other Elements on the Process.** This method is not affected by the presence of large amounts of aluminum, zinc, cadmium, calcium, or magnesium. Cobalt, manganese, and nickel in small amounts are not objectionable, but larger amounts affect the accuracy of the end point determination. Chromium in large amounts increases the difficulty of recognizing the point at which the proper excess of stannous chloride has been added, but in small amounts is not objectionable. Copper, since it is reduced to the cuprous form by stannous ion and reoxidized by dichromate ion, increases the amount of dichromate solution used almost in proportion to the amount present, and also masks the end point on account of the color of cupric ion. Pentavalent arsenic and antimony and tetravalent titanium are also reduced by stannous ion and partially oxidized by dichromate ion. If solutions containing either copper, arsenic, antimony, or titanium are reduced by hydrogen sulfide these errors are avoided since the three first-named elements are precipitated and can be removed by filtration, and the last is not reduced.

**Procedure for an Easily Soluble Hematite or Magnetite Ore.**

Weigh out 1 gram of the finely ground sample into a covered beaker, introduce 20 cc. of concentrated hydrochloric acid and 5 cc. of the stannous chloride solution, and allow to digest at a moderate temperature until the residue is white. Rinse the cover and sides of the beaker and transfer the solution to a 100-cc. graduated flask. Cool to room temperature, dilute to exactly 100 cc., and mix thoroughly. Remove by means of a pipette 25 cc. of the solution to a 250-cc. beaker, add 5 cc. of dilute hydrochloric acid, heat almost to boiling, and then add stannous chloride by means of a dropping tube until the mixture is just colorless. Cool the solution, add 80 cc. of water, and then 10 cc. of a saturated solution of mercuric chloride. This should produce a white silky precipitate of mercurous chloride.

Titrate with the dichromate solution as in the standardization, adding it in quantities of 2 cc. at a time until the tests show a change from deep blue to light blue, then add 1 drop at a time until the proper end point is reached. With some experience it is possi-

ble to obtain a good result with the first portion of solution used; beginners usually find it necessary to titrate a second portion. If the insoluble residue is dark colored, or if there is reason to believe it contains appreciable amounts of iron, it should be filtered out and washed, ignited in a crucible, and treated as a difficultly soluble ore.

**Procedure for a Difficultly Soluble Ore.** Weigh out into a 20-cc. glazed porcelain crucible approximately 3 grams of sodium peroxide, avoiding the white crust often found on the surface, which consists largely of sodium carbonate, and which, in addition to being less efficient in its action on the ore, has a much higher melting point. Weigh out accurately 1 gram of the finely powdered ore, add to the crucible, and mix with the peroxide by means of a dry glass rod. Heat the crucible continuously over a wire gauze until the contents fuse and keep slightly above the fusion point for a few minutes. This should yield a clear but deeply colored molten mass. Allow the crucible to cool, distributing the molten mass over its inner surface by careful tipping and rotating during solidification. Place the crucible in a 400-cc. beaker, cover with a watch glass, introduce 50 cc. of water, and stir until the fused mass is disintegrated. Then add a slight excess of hydrochloric acid. Remove and rinse off the crucible, heat the solution, and keep it near the boiling point until the hydrogen peroxide formed is completely decomposed. Transfer to a 100-cc. graduated flask and treat this solution as in the analysis of easily soluble ores.

### III. Determination of Chromium

**General Theory.** The reaction which takes place between a soluble chromate and ferrous ion in the presence of hydrogen ion can also be used for the determination of chromium by use of the method of back titration, that is, by adding a known amount of ferrous ion and then titrating the excess with a standard dichromate solution. Compounds which contain chromium in its lower stages of oxidation can be changed to soluble chromates by a number of reagents. In the presence of large concentrations of nitric acid or sulfuric acid soluble compounds of chromium are completely oxidized by chlorates, persulfates, and the dioxides

of lead and manganese. In the presence of bases they are oxidized by hypochlorites, hypobromites, and sodium peroxide. In devising a process for the determination of chromium based upon these two reactions it is necessary to use an oxidizing agent, the excess of which can be completely and readily eliminated before proceeding to the determination of the chromium formed.

**Decomposition of Chromite.** This mineral is a combination of the sesquioxide of chromium and certain basic oxides, especially ferrous oxide and magnesium oxide. Many samples also contain oxides of manganese, aluminum, and silicon. The mineral is practically unaffected by large concentrations of the mineral acids or by fusion with the hydrates and carbonates of the alkalis. Fusion in a nickel crucible with sodium peroxide gives rapid and complete decomposition, with the formation of soluble chromates, ferrates, manganates, aluminates, and silicates, and separation of insoluble oxides of magnesium and nickel, the latter derived from the crucible. The fused mass is rapidly disintegrated by treatment with water, especially if an excess of peroxide is present, with the formation of ferric hydroxide as a result of the hydrolysis of ferrates. Heating of the solution to the boiling point effects complete decomposition of the excess of peroxide and reduction of the manganates. The filtrate obtained by heating and filtering this mixture should contain all the chromium as chromate ion and no substances which affect the quantitative determination of the latter. Since the elements removed by the filtration do not seriously affect the accuracy of this titration some analysts add sufficient sulfuric acid to the mixture to make it distinctly acidic to dissolve the insoluble oxides, and thus eliminate the necessity of filtration.

**Procedure for the Determination of Chromium in Chromite.** Weigh out about 4 grams of sodium peroxide into a 30-cc. nickel crucible. Weigh out accurately 0.5 gram of the chromite, add to the crucible and mix thoroughly with the peroxide by means of a dry glass rod. Heat the crucible over a triangle until the mixture is brought to the fusion point and keep at this temperature for about five minutes. The resulting liquid mass will be of a dark red color but will not be clear owing to suspended nickel oxide. Allow the crucible to cool, distributing the contents around its

sides during solidification, then place in a 400-cc. beaker; add 150 cc. of water, cover with a watch glass, and stir until the melt is entirely disintegrated. Remove the crucible by means of a rod and rinse off with distilled water. Heat the beaker to the boiling point and keep at this temperature until the hydrogen peroxide is entirely decomposed as indicated by cessation of the liberation of oxygen gas. Allow the beaker to stand until the black precipitate, composed of ferric hydroxide, nickel oxide and manganese oxide, settles, then filter by means of an asbestos filter, and wash with three portions of wash water. Transfer the solution to a 250-cc. graduated flask and make slightly acid by the addition of sufficient dilute sulfuric acid to give the characteristic color of the dichromate ion. Allow to cool and dilute to exactly 250 cc. Measure out 50 cc. of the solution, add 5 cc. of concentrated hydrochloric acid, and then an excess of a standard solution of ferrous sulfate, or a weighed amount of pure ferrous sulfate; finally titrate the resulting mixture with the standard dichromate solution. Titrate a second portion of the solution as a check, and, finally, calculate the per cent of  $\text{Cr}_2\text{O}_3$  in the sample.

The asbestos filter should be transferred to a beaker and treated with a little warm dilute hydrochloric acid; if the precipitate associated with the asbestos does not dissolve completely it indicates that the decomposition of the sample was incomplete and a second fusion is necessary. There is little probability of incomplete decomposition if the directions given are followed, and if the sodium peroxide has not deteriorated as the result of absorption of water.

### Questions and Problems. Series 28

1. What volume of tenth normal dichromate solution would be reduced by 0.1 gram of iron when in the form of (a) metallic iron, (b) ferrous chloride, (c) the magnetic oxide? *Ans. (a) 53.71, (b) 17.91, (c) 5.97.*

2. If a solution of dichromate ion is tenth normal when used as an oxidizing agent, what relation does it bear to normality when used as a precipitating agent?

3. In the standardization of a tenth normal dichromate solution a solution of ferrous ion, which has a volume of 100 cc. and contains 0.2 gram of iron, is used. In titrating the solution obtained from 0.5 gram of a 40 per cent iron

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ore with the dichromate solution the volume before titration is 600 cc. If the indicator used is capable of detecting one part of ferrous iron in 100,000 what result would be obtained assuming that the only error is that due to the fact that the two titrations are made at different volumes?

*Ans.* 39.03 per cent.

4. What result should be expected in a determination of iron in an ore containing 40 per cent of iron and two-tenths per cent of copper, assuming that the copper is completely reduced by stannous to cuprous ion and reoxidized by dichromate ion?

*Ans.* 40.18 per cent.

5. Discuss all of the factors which determine the completeness of the reaction in which mercuric chloride is reduced by stannous ion.

6. How could you decide from the method used for the determination of iron in an iron ore whether dichromate ion should, under the proper conditions, oxidize stannous ion completely?

7. Write balanced equations for all the reactions representing the successive changes in the process used for the determination of chromium in chromite, assuming the sample is represented by the formula  $\text{FeCr}_2\text{O}_4$ .

8. Discuss the advantages and disadvantages of dissolving the precipitate of iron and nickel oxides obtained in the analysis of chromite by means of sulfuric acid rather than filtering them off before acidifying as in the procedure outlined.

9. What is the normality, as to oxidizing or reducing power, of a mixture composed of 24 cc. of 0.012 normal  $\text{FeSO}_4$ , 13 cc. of 0.006 normal  $\text{KMnO}_4$ , 15 cc. of 0.005 normal  $\text{K}_2\text{Cr}_2\text{O}_7$  and 30 cc. of 0.01 normal  $\text{H}_2\text{SO}_4$ ? *Ans.* 0.00164.

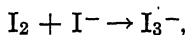
10. Calculate the concentrations of all the ions present in recognizable amounts in the mixture described in the preceding problem after equilibrium has been attained? *Ans.*  $\text{SO}_4^{--} = 0.00139$ ,  $(\text{H}^+) = 0.0012$ ,  $(\text{K}^+) = 0.00004$ ,  $(\text{Cr}^{+++}) = 0.000025$ ,  $(\text{Mn}^{++}) = 0.0000156$ .

## CHAPTER XXXVI

### DETERMINATIONS WITH SOLUTIONS OF TRI-IODIDE ION

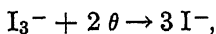
#### I. General Features of Iodimetric Processes

**Properties of Solutions of Tri-iodide Ion.** Although a solution of iodine in water is a satisfactory oxidizing agent its solubility is so small that it is not possible to prepare solutions whose concentration exceeds 0.00136 molal. Advantage is therefore taken of the fact that iodine and iodide ion readily form a complex ion whose oxidizing properties are almost identical with those of free iodine. The reaction corresponding to the expression

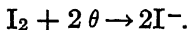


is determined by a constant whose value is 770, which is large enough to insure conversion of most of the iodine added to a solution containing the theoretically required amount of a soluble iodide into tri-iodide ion. Although the resulting tri-iodides are decidedly soluble but few of them have been prepared in solid form owing to the fact that when such solutions are concentrated solid iodine separates before saturation as to the tri-iodide is attained.

The electrode potential corresponding to the expression



has been found to have the value +.54 volt, which is 0.005 volt greater than for



The potential of the last reaction is considerably less than that of the two oxidizing agents already considered, and unlike that for these reagents, the action of tri-iodide ion is a reversible one.

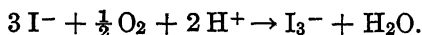
These facts indicate that the reactions in which tri-iodide ion is used should be less complete than those in which permanganate or dichromate ion are used. An additional difference is that tri-iodide ion does not require the consumption of hydrogen ion when reduced, and therefore some of the processes in which it is used are not affected by varying hydrogen-ion concentration. However, since the substance oxidized may either yield or consume hydrogen ion this is not true of all reactions in which tri-iodide ion is used.

In using tri-iodide ion as an oxidizing agent three possible sources of error must be kept in mind. First, tri-iodide ion hydrolyzes according to either of the two equations:



The electrode potential for the second of these processes has the value  $-.66$  volt and the tendency for the formation of iodate ion is therefore not large unless the value of  $(\text{H}^+)$  is kept at a very small figure by the addition of  $\text{OH}^-$ . The corresponding potential of the first process is  $-.91$  volt. In general, however, it is not desirable to use tri-iodide ion in solutions in which  $(\text{H}^+)$  is less than  $1 \times 10^{-7}$ .

Second, iodide ion, which is always present in excess in the tri-iodide solution actually used, in the presence of hydrogen ion is slowly oxidized by the oxygen of the atmosphere according to the equation



Although this reaction is decidedly slow its rate is greatly increased by large concentrations of  $\text{H}^+$  and by the presence of a large number of substances which act as catalysts. It is advisable, therefore, to make all titrations with tri-iodide solutions in mixtures in which  $(\text{H}^+)$  does not exceed  $1 \times 10^{-7}$ . If it is necessary to make the titration in strongly acidic solutions it should be completed as rapidly as possible or the solution should be kept in a flask in which the air has been replaced by carbon dioxide.



Third, the iodine of tri-iodide ion is appreciably volatile in solutions of tenth normal concentrations, even at 25° C. At higher temperatures the loss of iodine may cause rather large errors. The volatility of free iodine, which, owing to insufficient iodide ion, may separate in solid form from the solution, is still greater.

**Recognition of End Points.** The color of solutions containing  $I_2$  and  $I_3^-$  is of the same general character and at equal concentrations is of about the same intensity. A single drop (about .04 cc.) of tenth normal solution of tri-iodide ion imparts a perceptible yellow color to 200 cc., and if other colored ions are absent, it is possible to make accurate titrations with such solutions by ascertaining at what point the mixture being titrated acquires a recognizable color. If, however, a higher degree of accuracy is required, or if other colored ions are present, use can be made of the very intense blue color which is imparted to solutions containing  $I_3^-$  or  $I_2$  by the addition of soluble starch. The formation of this color seems to be due to a colloidal phenomenon and requires the presence of rather large concentrations of both iodide ion and of starch, as well as  $I_2$  and  $I_3^-$ . Its character varies somewhat; when the concentration of  $I_3^-$  is large compared with that of starch this color is green, but changes to blue as the concentration of  $I_3^-$  is reduced; if the solution is nearly neutral, and especially if it contains large concentrations of salts, the color is rose or purple. In preparing the starch solution the starch grains are heated with water to at least 80°. The heating causes them to burst and liberate soluble starch or  $\beta$ -amylose. On cooling, the insoluble  $\alpha$ -amylose slowly settles out. Since the latter is insoluble and gives rise to red rather than blue colors it is desirable to use the clear supernatant solution only. Furthermore,  $\beta$ -amylose, in the presence of moderate concentrations of hydrogen ion, undergoes hydrolysis with the formation of amyloextrine and related compounds. These substances give red rather than blue color reactions and do not react as decisively at the true end point. Starch solutions are also subject to fermentation through the action of various fungi and bacteria, which greatly affects their use as indicators. It is not desirable to use starch solutions which have stood for more than two or three days.

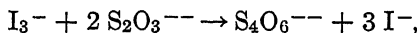
**Classification of Iodimetric Processes.** Iodimetric processes may be classified into three fairly definite groups. The first comprises processes based upon the direct oxidation of the substance determined. This includes the element tin, which is oxidized from the bivalent to the quadrivalent condition even in acid solution; arsenic and antimony, which are oxidized from the tri- to the quinquivalent condition in solutions in which ( $H^+$ ) is kept very small; sulfites, which are oxidized to sulfates in either neutral or acid solutions; sulfides which are oxidized to sulfur and hydriodic acid in neutral or acid solutions; thiosulfates, which are oxidized to tetrathionates in neutral solutions; and cyanides, which are oxidized to cyanogen iodide in neutral solutions.

The second group comprises processes based upon the reduction of the substance determined by iodide ion and the titration of the tri-iodide ion thus formed. The halogens  $Cl_2$  and  $Br_2$  and cupric ion are almost completely reduced, even when only a moderate excess of iodide ion is present; the reduction of ferric ion is much less complete. Many of the oxygen containing anions such as  $MnO_4^-$ ,  $BrO_3^-$ ,  $IO_3^-$  and  $Cr_2O_7^-$  are practically completely reduced even in the presence of only moderate concentrations of  $I^-$  and  $H^+$ ; others, such as  $AsO_4^{3-}$  and  $SbO_3^-$  require very large concentrations of both  $I^-$  and  $H^+$ ; and still others, such as  $MoO_4^{2-}$  and  $WO_4^{2-}$ , are not completely reduced unless the mixture is heated and the liberated iodine removed by distillation.

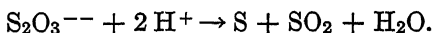
The third group comprises indirect processes which represent combinations of precipitation and oxidation processes. Thus, those metals which form insoluble chromates of definite composition can be determined by adding a measured volume of a standard solution of a soluble chromate, filtering off the precipitate formed and determining the chromate ion left in the filtrate. The amount of metal present can then be calculated from the difference between the soluble chromate added and that found in the filtrate.

**Solutions Needed for Iodimetric Determinations.** Iodometric determinations require the preparation of a standard solution of tri-iodide ion for the determination of reducing agents and of

some reagent which reacts readily and completely with tri-iodide ion for the determination of oxidizing agents. Since the concentration of the tri-iodide ion decreases on standing, even when protected against the action of sunlight, and must therefore be standardized at frequent intervals, it is desirable that the reducing agent chosen be a stable one. This requirement is most nearly satisfied by sodium thiosulfate, which is easily obtained in a high degree of purity as a solid which has the formula  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ . Solutions of it can be kept for several weeks without appreciable decomposition but in the presence of even small concentrations of hydrogen ion it is slowly decomposed with the formation of sulfur and sulfur dioxide. The reaction



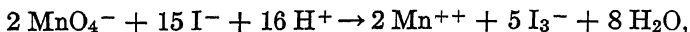
is not reversible and is practically complete where equivalent amounts of the two reagents are present. If the solution is alkaline some thiosulfate ion is oxidized to sulfate ion and even in a neutral solution the amount of tri-iodide ion used up is very slightly in excess of that theoretically required, which probably represents the formation of a very small amount of sulfate ion. This error is avoided by the presence of a very small concentration of hydrogen ion; a large excess should be avoided owing to the possibility of the reaction



Fortunately this reaction is slow at ordinary temperatures.

In the oxidation of thiosulfate to tetrathionate ion the average valence of each sulfur atom changes from plus two to plus two and one-half, which makes the equivalency of the thiosulfate ion one. A one-tenth normal solution is concentrated enough to give end points, with starch as an indicator, of a high degree of accuracy. The thiosulfate solution most frequently used therefore is made by dissolving 24.82 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$  in water and diluting to 1 liter. Since it is not easily possible to obtain samples which contain the theoretical percentage of water the solution is usually standardized by one of the methods described below.

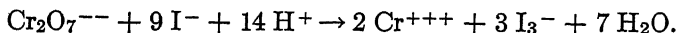
**Standardization with Permanganate Solution.** The addition of permanganate solution to a solution containing thiosulfate ion yields a variety of oxidation products and the process can not be expressed by any single equation. However, if the permanganate solution is added to a solution containing an excess of iodide ion and a proper concentration of hydrogen ion, an amount of tri-iodide ion corresponding almost exactly to the expression



is formed. The tri-iodide ion can then be accurately titrated with the thiosulfate solution being standardized. Since hydrogen ion is used up, the completeness and speed of the reaction depends upon its concentration. Large concentrations of hydrogen ion should be avoided because the rate at which the oxygen of the air forms tri-iodide ion becomes appreciable and it is then necessary to carry out the titration in a flask in which air is replaced by carbon dioxide. The concentration of iodide ion should be large enough to prevent solid iodine from separating and it is desirable to add the permanganate to the iodide solution rather than the reverse in order to avoid the temporary separation of solid iodine. If this takes place there is a possibility of loss from volatilization. It should also be noted that samples of potassium iodide frequently contain small amounts of iodates and such samples form tri-iodide ion when acidified. Unless iodates are known to be absent the solution of iodide and acid should first be prepared and any tri-iodide ion which may form must be reduced by cautiously adding the necessary amount of thiosulfate solution, before adding the permanganate solution. The following variations in the conditions under which this method was used were found<sup>1</sup> to yield results differing from the correct value by not more than 0.01 per cent: time allowed for reaction 0.3 to 10 minutes; volume during reaction, 75 to 600 cc.; potassium iodide used, 1.5–10 grams; sulfuric acid used, 0.005–0.06 equivalent; acid concentration during titration, 0.004–0.2 normal.

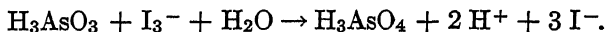
<sup>1</sup> Bray and Miller, Jour. Am. Chem. Soc., 46, 2217 (1924).

**Standardization with Dichromate Solution.** A similar method of standardization based upon the use of pure solid potassium dichromate, or of a standard solution of this salt, assumes completeness of the reaction:



This reaction is certainly slower and probably a little less complete than the corresponding permanganate reaction, and therefore needs a slightly larger concentration of hydrogen ion. The presence of the most desirable concentration of  $\text{H}^+$  may result in the formation of appreciable amounts of  $\text{I}_3^-$  by the oxygen of the air but the probability of error from this source can be reduced by diluting the solution as soon as the reduction of the dichromate ion is complete as the process does not reverse. The details of procedure which gave results<sup>1</sup> accurate to within 0.01 per cent are given on page 391.

**Standardization with Arsenious Oxide.** Arsenious oxide is easily obtained in a high degree of purity owing to the ease with which it can be purified by sublimation or recrystallization. Although moderately soluble it dissolves very slowly and much time can be saved by dissolving it in either hydrochloric acid or sodium hydroxide and neutralizing the resulting solution. The reaction which is made use of is expressed by the equation



The equilibrium constant, that is

$$(\text{H}_3\text{AsO}_4) \cdot (\text{H}^+)^2 \cdot (\text{I}^-)^3 \div (\text{H}_3\text{AsO}_3) \cdot (\text{I}_3^-),$$

has been calculated from electrode potential measurements<sup>2</sup> to be 0.07 at 25° C. At first sight it would seem to be impossible to use a reaction whose constant is as small as this as the basis of an accurate quantitative process. It will be noted however that in the expression for the equilibrium constant,  $(\text{H}^+)$  is raised to the second and  $(\text{I}^-)$  to the third power and therefore the completeness of the reaction can be enormously increased by making

<sup>1</sup> Bray and Miller, l.c.

<sup>2</sup> Luther, Zeit. Electrochemie, 13, 289 (1907).

these values small. The value of  $(I^-)$  can not be reduced below that needed to keep all the iodine present in solution and also insure a satisfactory end point with the starch indicator. The value of  $(H^+)$  can not be reduced below the point at which the formation of appreciable concentrations of  $IO_3^-$  is possible. By making certain simplifying assumptions it was found possible to calculate<sup>1</sup> that if the error of the process due to incomplete oxidation of the arsenic was to be kept below 0.001 per cent the value of  $(H^+)$  must be kept within  $1 \times 10^{-4}$  and  $1 \times 10^{-9}$ . This requires the presence of a buffer which is capable of taking up the  $H^+$  liberated during the progress of the reaction. A number of buffer mixtures which should insure maintenance of  $H^+$  within these limits can be made use of. One of the most convenient consists of a 0.12 molal solution of sodium bicarbonate saturated with carbon dioxide.

## II. Details of Procedure for Preparation and Standardization of Solutions

**Procedure for the Preparation of Solutions.** Prepare a one-tenth normal solution of tri-iodide ion by weighing out in a closed weighing bottle 12.69 grams of pure iodine and 20 grams of potassium iodide, which is free from iodate, and transferring the mixture by means of about 25 cc. of water to a 200-cc. beaker. Stir the mixture till the solids are completely dissolved, then transfer the solution to a liter flask and dilute to 1 liter. Pour the solution into a clean bottle made of colored glass or covered with opaque paper to reduce the action of light on the solution as much as possible. Prepare a tenth normal solution of sodium thiosulfate by weighing out 24.82 grams of the pure crystallized salt, dissolving in water and diluting to 1000 cc. Prepare starch indicator by mixing about 1 gram of starch, preferably potato starch, with 20 cc. of water in a small beaker until a smooth mixture is obtained and then pouring slowly and with constant stirring into a second beaker containing 200 cc. of boiling water. Keep the mixture near the boiling point for a few minutes, being careful to prevent

<sup>1</sup> Washburn, Jour. Am. Chem. Soc., 30, 31 (1908).

the residual starch from settling to the bottom; if it does so the beaker may crack. Allow the mixture to stand for several hours and then decant off the clear solution and discard the residue.

**Procedure for the Standardization of Thiosulfate with Permanganate Solution.** Prepare a solution composed of 3 grams of potassium iodide, 2 cc. of 6 N sulfuric acid and 100 cc. of water. If the mixture shows a perceptible yellow color add a sufficient number of drops of the thiosulfate solution to just decolorize it and then dilute to 300 cc. Next add from a pipette 25 cc. of accurately standardized tenth normal potassium permanganate and allow to stand for about a minute. Add the thiosulfate solution from a burette till the solution shows a very faint yellow color only, and then add about 2 cc. of the starch solution and continue the titration until the blue color just disappears. Calculate the normality of the thiosulfate solution from the normality of the permanganate and the volumetric ratio between the permanganate and thiosulfate solutions thus found.

**Procedure for the Standardization of Thiosulfate with Dichromate Solution.** Prepare in a 600-cc. beaker a mixture composed of 3 grams of potassium iodide, 3 cc. of 6 N hydrochloric acid and 100 cc. of water. If the mixture shows a perceptible yellow color add just sufficient thiosulfate solution to decolorize it, then add by means of a pipette 25 cc. of the standard one-tenth normal solution of potassium dichromate and allow to stand for ten minutes, preferably in the dark. Dilute the mixture to 500 cc. and titrate with the thiosulfate solution till most of the tri-iodide ion has been used up. This should require about 24 cc. of the thiosulfate solution and should yield a yellowish green mixture. Finally add 3 cc. of starch indicator and continue the titration till the mixture changes from blue to a very light green color. Calculate the normality of the thiosulfate solution from the relation thus found and the normality of the dichromate solution. If solid dichromate is weighed out for the determination not more than 0.2 gram should be used.

**Procedure for the Standardization of Tri-iodide Solution with Arsenious Oxide.** Weigh out 0.2 gram of pure arsenious oxide into a 400-cc. Erlenmeyer flask, add 20 cc. of approximately 0.5 normal sodium hydroxide and stir till the oxide is completely

dissolved. Add a drop of phenolphthalein indicator and then dilute hydrochloric acid till the solution has entirely lost its red color. Dilute to 75 cc., add 2.5 grams of sodium bicarbonate and pass carbon dioxide through it till saturated. Finally add 2 cc. of starch indicator and titrate with the tri-iodide solution added from a glass-stoppered burette until the mixture acquires a faint but permanent rose to purple color. Calculate the normality of the tri-iodide solution.

**Procedure for the Standardization of Thiosulfate with Tri-iodide Solution.** The action of light on the tri-iodide solution causes its normality to decrease slowly and makes it necessary to restandardize at frequent intervals, either by means of arsenious oxide or by means of the standard thiosulfate solution. In making the latter titration it will be found that the end points can be ascertained with a little greater degree of assurance if the tri-iodide solution is added to the thiosulfate rather than the reverse. Measure out by means of a pipette 25 cc. of the standard thiosulfate solution and place in a 250-cc. Erlenmeyer flask, dilute to 100 cc. and saturate with carbon dioxide; add 2 cc. of starch indicator and titrate with the tri-iodide solution till the solution shows a very faint but permanent blue color. Calculate the normality of the thiosulfate solution.

### III. Determination of Antimony

**General Theory.** Trivalent compounds of antimony are oxidized by tri-iodide ion under essentially the same conditions as the corresponding compounds of arsenic. Although the ideal conditions for the process have not been accurately determined tri-iodide ion forms the basis of a quantitative process which is by far the best volumetric method for the determination of this element. Pentavalent compounds of antimony, like those of arsenic, are completely reduced by iodide ion in the presence of large concentrations of hydrogen ion to trivalent compounds. Although this reduction by iodide ion has been used as the basis of quantitative procedures for the determination of both elements such procedures are less satisfactory than those based on the converse change reaction, that is, oxidation by tri-iodide ion.

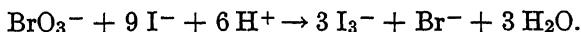


Important differences in the properties of the two elements result from the slightly weaker acidic character of the antimony and its greater tendency to form complexes, especially with certain organic acids such as tartaric, malic and oxalic. Its weaker acidity leads to the formation of insoluble basic compounds and it is not possible to reduce the value of  $(\text{H}^+)$  in a solution containing antimony to a value at which it can be completely oxidized by tri-iodide ion without causing partial precipitation, unless a sufficient concentration of one of the acids named is also present. The compound known as tartar emetic ( $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ ), which contains the basic antimonyl group  $\text{SbO}$ , is one of the most important commercial salts of antimony. It can be obtained in a high degree of purity<sup>1</sup> by recrystallization and has been used as a primary standard, but it is difficult to prepare and keep samples which contain the theoretical percentage of water.

**Procedure for the Determination of Antimony in Commercial Tartar Emetic.** Weigh out 0.4 to 0.5 gram of the sample into a 300-cc. Erlenmeyer flask, add about 1 gram of Rochelle salt,  $\text{C}_4\text{H}_4\text{Na}_2\text{KO}_6$  and 100 cc. of water and stir till both salts are dissolved. Next add 2.5 grams of pure sodium bicarbonate and saturate the mixture with carbon dioxide. Finally add 2 cc. of starch indicator and titrate with the tri-iodide solution till a faint but permanent purple color appears. Calculate the percentage of antimony present.

#### IV. Determination of Soluble Bromates

**General Theory.** Although bromate ion is, in the presence of hydrogen ion, a powerful oxidizing agent it does not oxidize thio-sulfate ion by a reaction which can be expressed by a single equation. It does, however, oxidize iodide to tri-iodide ion in accordance with the expression;



The concentration of hydrogen ion needed to make the reaction complete has not been accurately determined but is known to be

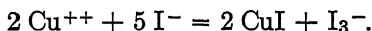
<sup>1</sup> Hale, Jour. Am. Chem. Soc., 24, 828 (1902).

small. Very good results can be obtained by the procedure outlined below.

**Procedure for the Determination of Potassium Bromate in Commercial Salt.** Prepare in a 300-cc. Erlenmeyer flask a mixture composed of 10 cc. of 6 N sulfuric acid, 3 grams of potassium iodide and 50 cc. of water. If a yellow color appears add just enough drops of thiosulfite solution to destroy the color. Weigh out accurately from 0.1 to 0.2 gram of the sample, add to the mixture in the flask and allow to stand for two minutes. Dilute to 150 cc. and titrate with the thiosulfate solution until the mixture is nearly colorless; then add 2 cc. of starch indicator and continue the titration until the last traces of blue color has been destroyed. Calculate the percentage of potassium bromate present.

## V. Determination of Copper

**Theory of the Method.** This process is based upon the oxidation of iodide to tri-iodide ion by cupric ion and titration of the tri-iodide with standard thiosulfate solution. It assumes completeness of the reaction:



The table of electrode potentials gives the value 0.17 volt for the reduction of cupric ion to cuprous ion when both ions are at molal concentration but the value is 0.85 volt when the very slightly soluble cuprous iodide is present. Since oxidation of iodide to triiodide ion gives  $-.54$  volt the electromotive force of the reaction is 0.31 volt. This is sufficiently large to insure practically complete reduction of cupric ion if a moderate excess of iodide ion is present. Furthermore the removal of the liberated tri-iodide ion by titration with the thiosulfate solution insures a practically complete conversion of all the cupric to cuprous ion.

Experimental work has shown that the reaction is peculiarly sensitive to variations in the relative amounts of cupric salt and iodide used. The maximum amount of copper is precipitated and of tri-iodide ion is formed when a moderate but not excessive amount of soluble iodide is added. If the amount of copper present does not exceed 0.2 gram the use of 3 grams of potassium

iodide and a final volume of about 100 cc. gives good results.<sup>1</sup> A number of other strong electrolytes affect the process similarly. This may be attributed to the formation of complex ions since the cuprous ion is a decidedly weak ion, or of undissociated cupric iodide, although this salt has never been separated in solid form. It has also been shown that the separated precipitate may contain large amounts of insoluble polyiodides, such as  $\text{CuI}_3$ , which slowly form normal cuprous iodide, as the excess of tri-iodide ion is used up by the thiosulfate added. This reaction delays somewhat the completion of the reaction.

Although hydrogen ion does not take part in the reaction, a moderate concentration of it increases the rate at which equilibrium is attained and prevent the separation of insoluble basic compounds through hydrolysis. Obviously oxidizing agents which also liberate tri-iodide ion must be absent.

Since the ideal conditions under which this process should be carried out are known only approximately, and since pure metallic copper is easily obtainable, there is abundant justification for the custom, which prevails in commercial laboratories in which this method is largely used, of standardizing the thiosulfate solution by pure copper rather than by the methods already described. If the same details of procedure are used in the standardization as in the actual determination the errors resulting from the incompleteness of the reaction are largely eliminated.

**Procedure for the Determination of Copper in Brass.** Weigh out 0.3 gram of the sample into a 200-cc. Erlenmeyer flask, add 10 cc. of dilute nitric acid, warm slightly until the alloy is entirely dissolved, and then evaporate on a sand bath till the volume is reduced to about 3 cc. Add 50 cc. of water, and, if basic salts remain undissolved, add strong nitric acid drop by drop until they are dissolved. Next add ammonium hydroxide till the characteristic deep blue color of the cupric-ammonium complex ion appears, then sufficient dilute acetic acid to change the color to that of the cupric ion, and finally 3 cc. of acid in excess. Cool the solution to 20° C. and add 3 grams of potassium iodide, which is known to be free from iodate. Titrate the mixture with the

<sup>1</sup> Herschkowitsch, *Zeit. anorg. Chem.*, 146, 132 (1925).

thiosulfate solution until it has a slight yellow color only, then add 2 cc. of starch indicator and continue the titration until the light blue or lilac color is removed and the residual cuprous iodide precipitate is of a nearly white color. Calculate the percentage of copper.

The zinc in the sample, since it exists in one degree of oxidation only, should not effect the accuracy of the process. The tin, since it is oxidized by nitric acid to stannic ion or to insoluble metastannic acid also has a negligible effect on the process. The lead may form insoluble yellow lead iodide and mask the end point somewhat if the percentage is large.

**Procedure for the Determination of Copper in Ore.** Weigh out 1 gram, or if the sample contains more than 15 per cent, 0.5 gram of the ore into a 200-cc. Erlenmeyer flask, add 5 cc. of concentrated nitric acid, and warm till violent action is over. Next add 10 cc. of concentrated hydrochloric acid, evaporate till the volume has been reduced one-half, then cool. Add very cautiously 8 cc. of concentrated sulfuric acid and evaporate on a sand bath until the flask is filled with dense white fumes of sulfur trioxide. Cool the flask, add 30 cc. of water and allow to stand with occasional shaking until all soluble salts have been brought into solution. Transfer the solution to a 200-cc. beaker, retaining the insoluble matter as far as possible in the flask but washing it free from copper salt. The final volume should not exceed 70 cc. Add to the solution a strip of aluminum foil 3 cm. wide and 15 cm. long which has been bent into the form of the letter S, heat to 80° C. and set aside in a warm place until the copper is completely precipitated. This usually requires ten minutes longer than the time required to decolorize the solution. The rate of precipitation is retarded by the presence of ferric ion and increased by sulfuric acid which causes the liberation of sufficient hydrogen to stir the solution. Next add 10 cc. of water saturated with hydrogen sulfide, and, if the solution remains colorless or acquires a slight brown or black color only, filter at once, using a small filter and retaining as much of the precipitated copper in the beaker as possible. Wash the precipitate three times with 10 cc. portions of hydrogen sulfide solution. If the appearance of the mixture indicates incomplete precipitation of

the copper it may be necessary to saturate it with hydrogen sulfide gas.

Place the beaker containing the precipitate under the funnel and pour over the filter about 10 cc. of warm dilute nitric acid, moving the beaker in such a manner as to cause the acid solution to flow over the surface of the aluminum plate, and dissolve completely the adhering precipitate. Replace the beaker by the flask used to dissolve the ore, which in the mean time has been cleaned. Warm the solution in the beaker until all of the precipitate has been dissolved, then remove and rinse off the aluminum plate, pour the solution through the filter and wash it free from copper.

Add 10 cc. of bromine water to the flask and boil vigorously until the excess added is expelled. Cool the solution, make alkaline with ammonium hydroxide, acidify with acetic acid and then add 3 cc. of the dilute acid in excess. The solution should have a volume not greatly exceeding 60 cc.

Add 3 gm. of potassium iodide and titrate as in the previous determination, remembering that slightly more time must be allowed for the mixture to come to equilibrium owing to the smaller concentration of hydrogen ion present.

### Questions and Problems. Series 29

1. Calculate approximately the fraction of unreduced iodine present as the tri-iodide ion in a one-tenth normal solution when prepared as directed on page 390, assuming that the constant for the formation of tri-iodide ion is 770.

*Ans.* 0.982.

2. It is possible that when a perfectly neutral solution of thiosulfate ion is titrated with a solution of tri-iodide ion a very small quantity of sulfate ion is formed; write the balanced equation for the process. If in standardizing a thiosulfate solution which is exactly 0.1 normal, with a standard iodine solution, 1 per cent of the thiosulfate is oxidized to sulfate, what normality would be found for the thiosulfate solution?

*Ans.* 0.0934.

3. Write the balanced ionic equation for the reduction of iodate to tri-iodide ion by means of hydrogen ion and iodide ion. This reaction is complete as far as either iodate iodide or hydrogen ions are concerned if the other ions are present in moderate excess. Calculate the weight of sulfuric acid corresponding to 1 cc. of a tenth normal thiosulfate solution when the tri-iodide ion resulting from a limited amount of sulfuric is titrated with thiosulfate ion.



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TABLE IV. ATOMIC WEIGHTS.\*

	Sym- bol	Atomic Number	Atomic Weight		Sym- bol	Atomic Number	Atomic Weight
Aluminum...	Al	13	26.97	Mercury.....	Hg	80	200.61
Antimony...	Sb	51	121.77	Molybdenum..	Mo	42	96.0
Argon.....	A	18	39.94	Neodymium..	Nd	60	144.27
Arsenic.....	As	33	74.96	Neon.....	Ne	10	20.183
Barium.....	Ba	56	137.37	Nickel.....	Ni	28	58.69
Beryllium...	Be	4	9.02	Nitrogen.....	N	7	14.008
Bismuth.....	Bi	83	209.00	Osmium.....	Os	76	190.8
Boron.....	B	5	10.82	Oxygen.....	O	8	16.00
Bromine.....	Br	35	79.916	Palladium.....	Pd	46	106.7
Cadmium.....	Cd	48	112.41	Phosphorus...	P	15	31.027
Calcium.....	Ca	20	40.07	Platinum.....	Pt	78	195.23
Carbon.....	C	6	12.000	Potassium.....	K	19	39.096
Cerium.....	Ce	58	140.25	Praseodymium	Pr	59	140.92
Cesium.....	Cs	55	132.81	Radium.....	Ra	88	225.95
Chlorine.....	Cl	17	35.457	Radon.....	Rn	86	222.
Chromium...	Cr	24	52.01	Rhodium.....	Rh	45	102.91
Cobalt.....	Co	27	58.94	Rubidium.....	Rb	37	85.44
Columbium...	Cb	41	93.1	Ruthenium....	Ru	44	101.7
Copper.....	Cu	29	63.57	Samarium.....	Sm	62	150.43
Dysprosium...	Dy	66	162.46	Scandium.....	Sc	21	45.10
Erbium.....	Er	68	167.7	Selenium.....	Se	34	79.2
Europium...	Eu	63	152.0	Silicon.....	Si	14	28.06
Fluorine.....	F	9	19.0	Silver.....	Ag	47	107.880
Gadolinium..	Gd	64	157.26	Sodium.....	Na	11	22.997
Gallium.....	Ga	31	69.72	Strontium....	Sr	38	87.63
Germanium...	Ge	32	72.60	Sulfur.....	S	16	32.064
Gold.....	Au	79	197.2	Tantalum.....	Ta	73	181.5
Hafnium.....	Hf	72	178.6	Tellurium....	Te	52	127.5
Helium.....	He	2	4.002	Terbium.....	Tb	65	159.2
Holmium.....	Ho	67	163.5	Thallium.....	Tl	81	204.39
Hydrogen...	H	1	1.008	Thorium.....	Th	90	232.15
Indium.....	In	49	114.8	Thulium.....	Tm	69	169.4
Iodine.....	I	53	126.932	Tin.....	Sn	50	118.70
Iridium.....	Ir	77	193.1	Titanium.....	Ti	22	47.90
Iron.....	Fe	26	55.84	Tungsten.....	W	74	184.0
Krypton.....	Kr	36	82.9	Uranium.....	U	92	238.17
Lanthanum...	La	57	138.90	Vanadium.....	V	23	50.96
Lead.....	Pb	82	207.22	Xenon.....	Xe	54	130.2
Lithium.....	Li	3	6.940	Ytterbium....	Yb	70	173.6
Lutecium...	Lu	71	175.0	Yttrium.....	Y	39	88.92
Magnesium...	Mg	12	24.32	Zinc.....	Zn	30	65.38
Manganese...	Mn	25	54.93	Zirconium....	Zr	40	91.22

\* From the thirty-fourth annual report of the Committee on Atomic Weights, Jour. Am. Chem. Soc., 50, 615 (1928).